Advanced Functional Materials for Energy Related Applications
UNIVERSITY OF CALIFORNIA
RIVERSIDE

Advanced Functional Materials for Energy Related Applications

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

Koroush Sasan

June 2015

Dissertation Committee:

Dr. Pingyun Feng, Chairperson
Dr. Christopher Bardeen
Dr. Richard Hooley
The Dissertation of Koroush Sasan is approved:

________________________________________

________________________________________

________________________________________

Committee Chairperson

University of California, Riverside
Acknowledgements

I would like to take this opportunity to express my sincere gratitude and respect to Professor Pingyun Feng, for her guidance and enthusiasm. I deeply appreciate her inspiring ideas, continuous support and kindly encouragement, without which, this dissertation would not have been possible. She demonstrated the dedication and rigorous attitude toward science, which will inspire and benefit me for the rest of my life.

I greatly appreciate Dr. Krassimir N. Bozhilov in Department of Earth Science at UCR for structure and morphology analysis. I also would like to thank Dr. Dan Borchardt in Department of Chemistry at UCR for the EPR training and spectra investigation, I deeply appreciate Prof. Xianhui Bu at CSULB for his valuable suggestion, discussion and encouragement.

Over the past five years, I have also been very fortunate to have the opportunities to work together with the excellent members in Dr. Feng’s group: Dr. Quanguo Zhai, Dr. Tao Wu, Dr. Xiang Zhao, Dr. Le Wang, Dr. Jikai Liu, Dr. Qipu Lin, Dr. Aiguo Kong, Fei Bu, Chengyu Mao, Xitong Chen, and Yuan Wang who help me in many ways.

I am also very grateful to the rest of my dissertation committee, Prof. Christopher Bardeen and Prof. Richard Hooley, for their valuable comments on my dissertation.

There are many others who deserve many thanks. I would like to thank the staff in Department of Chemistry for their kindly service and help.
Finally, I want to sincerely thank my parents, my sister Franoosh and my brother Kiarash for everything they have done for me. Without their love, encourage and support, I could not finish my Ph. D. study smoothly.
Dedication

To my dad Sfandyar and my mom Shahnaz
ABSTRACT OF THE DISSERTATION

Advanced Functional Materials for Energy Related Applications

by

Koroush Sasan

Doctor of Philosophy, Graduate Program in Chemistry
University of California, Riverside, June 2015
Dr. Pingyun Feng, Chairperson

The current global heavy dependency on fossil fuels gives rise to two critical problems: I) fossil fuels will be depleted in the near future; II) the release of green house gas CO$_2$ generated by the combustion of fossil fuels contributes to global warming. To potentially address both problems, this dissertation documents three primary areas of investigation related to the development of alternative energy sources: electrocatalysts for fuel cells, photocatalysts for hydrogen generation, and photoreduction catalysts for converting CO$_2$ to CH$_4$.

Fuel cells could be a promising source of alternative energy. Decreasing the cost and improving the durability and power density of Pt/C as a catalyst for reducing oxygen are major challenges for developing fuel cells. To address these concerns, we have synthesized a Nitrogen-Sulfur-Iron-doped porous carbon material. Our results indicate that the synthesized catalyst exhibits not only higher current density and stability but also higher tolerance to crossover chemicals than the commercial Pt/C catalyst. More importantly, the synthetic method is simple and inexpensive.
Using photocatalysts and solar energy is another potential alternative solution for energy demand. We have synthesized a new biomimetic heterogeneous photocatalyst through the incorporation of homogeneous complex 1 [(i-SCH$_2$)$_2$NC(O)C$_5$H$_4$N]-Fe$_2$(CO)$_6$] into the highly robust zirconium-porphyrin based metal-organic framework (ZrPF). As photosensitizer ZrPF absorbs the visible light and produces photoexcited electrons that can be transferred through axial covalent bond to dinuclear complex 1 for hydrogen generation.

Additionally, we have studied the photoreduction of CO$_2$ to CH$_4$ using self-doped TiO$_2$ (Ti$^{3+}@$TiO$_2$) as photocatalytic materials. The incorporation of Ti$^{3+}$ into TiO$_2$ structures narrows the band gap, leading to significantly increased photocatalytic activity for the reduction of CO$_2$ into renewable hydrocarbon fuel in the presence of water vapor under visible light.

Finally, we demonstrate that open-framework chalcogenides can also be used as efficient photocatalysts for the reduction of CO$_2$ to CH$_4$. These materials contain covalent superlattices of nanosized supertetrahedral clusters, which can be made with different metal cations to provide high electrical conductivity and current density as well as materials with different band gaps. The ability in incorporating different metal cations further enhances the material’s photocatalytic activity, which could possibly provide alternative technologies for reducing CO$_2$ in the atmosphere and simultaneously producing fuel.
# Table of Contents

Acknowledgement.................................................................................................................. iv  

Abstract..................................................................................................................................... vii  

Table of Contents.............................................................................................................................. ix  

List of Figures.................................................................................................................................. xiv  

Chapter 1. An overview of functional materials for energy-related applications.........1  
  1.2 Photocatalyst for hydrogen generation.............................................................. 1  
  1.2 Fuel cell ......................................................................................................................... 4  
  2.3 Photoreduction of CO₂ ............................................................................................. 6  
  1.4 References .................................................................................................................... 9  

Chapter 12. Incorporation of Iron Hydrogenase Active-Site into Highly Stable Metal–Organic Framework to Enhance Hydrogen Generation..............................................12  
  2.1 Introduction .................................................................................................................. 12  
  2.2 Experimental section ................................................................................................. 16  
    2.2.1 Chemicals and Instrumentation ........................................................................ 16  
    2.2.2 Synthesis of complex Fe₂S₂(CO)₆ ...................................................................... 16  
    2.2.3 Synthesis of complex [(f-SCH₂)₂NH]Fe₂(CO)₆................................................ 17
2.2.4 Synthesis of Complex 1[(i-SCH)\textsubscript{2}NC(O)C\textsubscript{5}H\textsubscript{4}N]-Fe\textsubscript{2}(CO)\textsubscript{6}]. .......................... 18

2.2.5 Synthesis of tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCPP). 18

2.2.6 Synthesis of ZrPF ........................................................................................................................................... 19

2.2.7 Photocatalytic experiment .................................................................................................................................. 20

2.3.1 High Stability of ZrPF ........................................................................................................................................ 21

2.3.3 BET and XRD measurement of [FeFe]@ZrPF .................................................................................................. 22

2.3.4 Fluorescence emission of [FeFe]@ZrPF ........................................................................................................... 23

2.3.6 ICP and EDX measurement .................................................................................................................................. 26

2.4 Result and dissection of photocatalyst ................................................................................................................ 27

2.5 Conclusion ............................................................................................................................................................ 29

2.6 References .............................................................................................................................................................. 31

Chapter 3 From Hemoglobin to Porous N-S-Fe-Doped Carbon for Efficient Oxygen Electroreduction .................................................................................................................................................................... 34

3.1 Introduction ............................................................................................................................................................... 34

3.2 Experimental section .................................................................................................................................................. 37

3.2.1 Chemicals and instrumentation ............................................................................................................................ 37

3.2.2 Synthesis catalysts ................................................................................................................................................ 38

3.2.3 Electrochemistry experiment .................................................................................................................................. 39

3.2.4 Koutecky-Levich experiment .................................................................................................................................. 39
3.3 Characterization of ORR catalysts ................................................................. 41

3.3.1 SEM and TEM images .............................................................................. 41

3.3.2 The surface area and pore size of Fe/N/S-C-4........................................... 43

3.3.3 The XPS measurement of Fe/N/S-C-4 ....................................................... 44

3.4 Electrocatalytic activity of Fe/N/S-C’s .......................................................... 46

3.4.1 Cyclic voltammetry (CV) measurement..................................................... 46

3.4.2 Linear sweep voltammetry (LSV) measurement......................................... 47

3.4.3 Influence of annealing temperature on the ORR activity ............................ 48

3.4.4 Influence of MS ratio on the ORR activity ................................................ 48

3.4.5 Resistance of the Fe/N/S-C-4 to crossover effect ...................................... 49

3.4.6 The durability of the Fe/N/S-C-4............................................................... 50

3.5 Result and dissection .................................................................................... 51

3.6 Conclusion .................................................................................................... 53

3.7 References .................................................................................................... 55

Chapter 4_Self-doped Ti$^{3+}$-TiO$_2$ as Photocatalyst for the Reduction of CO$_2$ into Hydrocarbon Fuel under Visible Light ................................................................. 58

4.1 Introduction .................................................................................................. 58

4.2 Experimental section ................................................................................... 61

4.2.1 Synthesis of self-doped Ti$^{3+}$-TiO$_2$ ........................................................ 61
Chapter 4

4.2.2 Characterization of self-doped Ti$^{3+}$-TiO$_2$.............................. 61
4.2.3 Photoreduction of CO$_2$.............................................................. 62
4.2.4 Flat-band potential measurement................................................. 63
4.3 Results ........................................................................................... 65
  4.3.1 Hydrothermal reaction................................................................. 65
  4.3.2 EPR and XRD results ................................................................. 65
  4.3.3 UV/vis absorption spectra and XPS measurement ...................... 66
  4.3.4 Co-catalyst effect ........................................................................ 68
  4.3.5 Photoreduction of CO$_2$ to CH$_4$................................................ 70
4.4 Discussion ...................................................................................... 72
4.5 Conclusion ..................................................................................... 75
4.6 References .................................................................................... 76

Chapter 5

5.1 Introduction .................................................................................... 79
5.2 Experimental section ..................................................................... 82
  5.2.1 Chemicals and instrumentation .................................................. 82
  5.2.2 Synthesis of AEM@GeZnS cluster ............................................. 83
  5.2.3 Preparation of film of AEM@GeZnS deposited on FTO electrode .... 84
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.3</td>
<td>Photoelectrochemical measurements</td>
<td>85</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Photoreduction of CO$_2$</td>
<td>85</td>
</tr>
<tr>
<td>5.3</td>
<td>Results</td>
<td>86</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Characterization of AEM@GeZnS</td>
<td>86</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Ion-exchange</td>
<td>87</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Photoelectrochemical response of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.</td>
<td>89</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Electrochemical impedance spectra (ESI) of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.</td>
<td>90</td>
</tr>
<tr>
<td>5.3.5</td>
<td>Photocatalyst result</td>
<td>91</td>
</tr>
<tr>
<td>5.4</td>
<td>Discussion</td>
<td>92</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusion</td>
<td>93</td>
</tr>
<tr>
<td>5.6</td>
<td>References</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Chapter Appendix</td>
<td>96</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1-1 Photocatalyst for hydrogen generation.................................................. 1
Figure 1-2 Several biomimetic [Fe₂S₂] complexes linked porphyrin as photosensitizers. 3
Figure 1-3 Fuel cell scheme.¹⁵b ............................................................................. 5
Figure 1-4 Photoreduction of CO₂........................................................................... 7
Figure 2-1. H₂ production by using sunlight and [FeFe]-H₂ase. Reprinted with permission from ref 5 Copyright 2012 American Chemical Society ........................................ 12
Figure 2-2. Model structure of MOF-Pt, through post-synthetic modification of MOF with PtCl₂.³⁰ ........................................................................................................ 14
Figure 2-3. a) Model structure of biomimetic [Fe₂S₂] complex 1 and b) Model structure of zirconium-porphyrin MOF (ZrPF). Color scheme: Zr drack green, Zn orange, C gray, O red, N blue, Fe green, S yellow. ................................................................. 15
Figure 2-4. (a) tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCPP). (b) The ZnTCPP is connected to four 8-connected Zr₆ clusters to generated secondary building units of Zr₆O₈(CO₂)₈(H₂O)₈. (c) zirconium-prophyrin MOF (ZrPF). Color scheme: Zr drack green, Zn orange, C gray, O red, N blue, Fe green, S yellow. ......................... 19
Figure 2-5. The scheme of setup for the photocatalytic water splitting........................ 20
Figure 2-6. PXRD of ZrPF in acidic solutions (pH = 5 for 24 h) and exposure to visible light (>420 nm). ........................................................................................................ 21
Figure 2-7. Complex 1 [(i-SCH₂)₂NC(O)C₅H₄N]-Fe₂(CO)₆. (e) [FeFe]@ZrPF (complex1- ZrPF)................................................................................................................. 22
Figure 2-8. (a) PXRD of Simulated of ZrPF, MO-ZP and [FeFe]@ZrPF. (b) N₂ absorption and desorption isotherms for ZrPF and [FeFe]@ZrPF. ........................................... 23

Figure 2-9. Normalized fluorescence spectra of ZrPF and [FeFe]@ZrPF. ....................... 24

Figure 2-10. FTIR of ZrPF, Complex 1 and [FeFe]@ZrPF. ........................................... 25

Figure 2-11. a) SEM and EDX analysis of ZrPF and b) SEM and EDX analysis of [FeFe]@ZrPF. ................................................................................................................................. 26

Figure 2-12. Photocatalytic hydrogen production in the presence of [FeFe]@ZrPF (black trace, ~2 μM), complex 1 (red, ~2 μM), ZrPF (blue). Reaction condition pH 5 (1.0 M acetate buffer solution), Visible light (> 420 nm) and 20 Mmol ascorbic acid. ............... 28

Figure 2-13. H₂ production by using sunlight and [FeFe]@ZrPF. ............................... 30

Figure 3-1 Alkali fuel cells operate on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte. 34

Figure 3-2 The X-ray crystal structures of hemoglobin. Reprinted with permission from ref 4b Copyright 1996. American Chemical Society.............................................. 35

Figure 3-3 The ORR catalyst from pyrolysis of an iron-coordinated complex with nitrogen rich ligand. Reprinted with permission from ref 7 Copyright 2014 American Chemical Society ........................................................................................................ 36

Figure 3-4 K–L plot of J-1 versus ω-1 at different potential of Fe/N/S-C-4 ....................... 41

Figure 3-5 a). The SEM image and b) the TEM image of Fe/N/S-C-4. ............................ 42

Figure 3-6 The SEM image, EDX and SEM-EDS elemental mapping image of Fe/N/S-C-4................................................................................................................................. 42
Figure 3-7 Adsorption–desorption isotherm of Fe/N/S-C-0, Fe/N/S-C-2 and Fe/N/S-C-4.

43

Figure 3-8 a) XPS spectra survey scan and b) high-resolution N1s of Fe/N/S-C-4 ........ 45

3-9 The high-resolution of a) C1s and b) S2p of Fe/N/S-C-4 ........................................ 45

Figure 3-10 CVs for various catalysts obtained under different mass ratios of sucrose to TCA........................................................................................................................................ 46

Figure 3-11 (a) LSV curves for various catalysts and a Pt/C catalyst at a rotation rate of 1600 rpm, (b) LSV curves for various rotating speeds for Fe/N/S-C-4................................. 47

Figure 3-12 LSV curves at a rotation rate of 1600 rpm for various catalysts obtained under different annealing temperature. .................................................................................. 48

Figure 3-13.a) LSV curves for various carbon materials, Hemoglobin (Black), Hemoglobin+TCA (Red), Fe/N/S-C-0 (Blue) and Fe/N/S-C-4 (Green) on a glass carbon rotating disk electrode in O₂-saturated 0.1 M KOH, 1600 rpm. b) LSV curves for various MS ratio, black (400mg Hem/1600mg TCA/No MS), red (400mg Hem/1600mg TCA/500mg MS), blue (400mg Hem/1600mg TCA/1000mg MS) and green (400mg Hem/1600mg TCA/2000mg MS) on a glass carbon rotating disk electrode in O₂-saturated 0.1 M KOH, 1600 rpm ........................................................................................................ 49

Figure 0-14 Chronoamperometric responses of Fe/N/S-C-4 and Pt/C catalyst with 3 M methanol added at around 360 s ........................................................................................................ 50

Figure 3-15 Chronoamperometric responses of Fe/N/S-C-4 and Pt/C catalyst, at -0.40 V in an O₂-saturated 0.1 M KOH solution .......................................................................................... 51
Figure 3-16 The Fe/N/S-C-4 has been formed through a convenient, economical, and scalable route. .............................................................. 54

Figure 4-1 The solar radiation spectrum for direct light at both the top of the Earth's atmosphere and at sea level. ................................. 60

Figure 4-2 a) Photograph of the reaction chambers set in the sunlight. Reprinted with permission from ref 18a Copyright 2009 American Chemical Society b) Our designed system. .................................................................................. 62

Figure 4-3 Mott-Schottky plot obtained at different frequencies for Ti$^{3+}$-TiO$_2$. .......... 64

Figure 4-4 a) EPR spectra measured at 100 K. b) XRD patterns for the Ti$^{3+}$-TiO$_2$ ........ 66

Figure 4-5 The Ti 2p XPS spectra of the Ti$^{3+}$-TiO$_2$. No Ti$^{3+}$ signal (at 456.6 eV) was detected. ........................................................................................................ 67

Figure 4-6 UV/Vis diffuse reflectance spectra for commercial P25 (red) and Ti$^{3+}$-TiO$_2$ (black). ........................................................................................................ 67

Figure 4-7 The Pd 3d XPS spectra of the Pd/Ti$^{3+}$-TiO$_2$........................................... 68

Figure 4-8 The Cu 2p XPS spectra of the Cu$^+/Ti^{3+}$-TiO$_2$ and the Cu$^+/Pd/Ti^{3+}$-TiO$_2$...... 69

Figure 4-9. The TEM image of a Pd@Cu/Ti$^{3+}$-TiO$_2$, nanoparticles found on the {111} facets ........................................................................................................ 70

Figure 4-10 The CH$_4$ formation under different co-catalysts on Ti$^{3+}$-TiO$_2$, no co-catalyst (black), Cu$^+$ (green), Pd (brown) and Cu$^+/Pd$ (blue). ..................................................... 71

Figure 4-11 The CH$_4$ formation under different photocatalyst, P25 (black), RC-TiO$_2$ (red) and Ti$^{3+}$-TiO$_2$ (blue). ................................................................. 72

Figure 4-12 Flat-band and conduction band of the Ti$^{3+}$-TiO$_2$. ................................. 73
Figure 4-13  N\textsubscript{2} adsorption-desorption isotherms of Ti\textsuperscript{3+}-TiO\textsubscript{2} from hydrothermal and
RC-TiO\textsubscript{2} from combustion method............................................................................................................. 74

Figure 4-14  Photoreduction of CO\textsubscript{2} with a partially reduced non-stoichiometric rutile
TiO\textsubscript{2} with active facets...................................................................................................................................... 75

Figure 5-1  Photoreduction of CO\textsubscript{2} and carbon cycle.\textsuperscript{5} ................................................................. 80

Figure 5-2 Three-dimensional framework of AEM@GeZnS the blue sphere represent the
void inside the cage. Color scheme, S green and Ge/Zn purple. ................................................................. 81

Figure 5-3 Photographes of AEM@GeZnS. Reprinted with permission from ref 17b
copyright 2015 American Chemical Society. (Photo credit: Qipu Lin)................................. 84

Figure 5-4 Thermogravimetric analysis (TGA) of AEM@GeZnS................................................................. 86

Figure 5-5 PXRD of Simulated of AEM@GeZnS, AEM@GeZnS, Pd@GeZnS and
Au@GeZnS......................................................................................................................................................... 88

Figure 5-6 Transient photocurrent density versus time plotted for the electrodes
functionalized with the ground materials of AEM@GeZnS, Pd@GeZnS and
Au@GeZnS......................................................................................................................................................... 89

Figure 5-7 (a) Nyquist plots of the three electrodes in dark, (b) and at present of light... 90

Figure 5-8 Three cycle experiments of CO\textsubscript{2} photoreduction into CH\textsubscript{4}. Using O.2 g of
photocatalysts (three clusters) under UV-Vis light......................................................................................... 91

Figure 6-1 PXRD of Simulated of ZrPF (Black), ZrPF (blue) and [FeFe]@ZrPF (red). 96

Figure 6-2 TGA of ZrPF (black) and [FeFe]@ZrPF (red)..................................................................................... 97
Figure 6-3  FTIR spectrum of heterogeneous catalyst [FeFe]@ZrPF upon exposure to visible light. Catalyst before exposure to visible light (Black) and after exposure to visible light for 40 mins (red) ................................................................. 97

Figure 6-4 The possible mechanism [FeFe]@ZrPF photocatalyst. ........................................ 98

Figure 6-5 The pure Complex 1 [(i-SCH2)2NC(O)C5H4N]-Fe2(CO)6] after sublimation .................................................. 98

Figure 6-6 XRD patterns for the Fe/N/S-C-4. ........................................................................... 99

Figure 6-7 N2 adsorption-desorption isotherms of Fe/N/S-C-6............................................ 99

Figure 6-8 Pore size distribution of Fe/N/S-C-0 and Fe/N/S-C-4. .................................... 100

Figure 6-9 SEM image of Fe/N/S-C-0......................................................................................... 100

Figure 6-10 SEM image of Fe/N/S-C-6......................................................................................... 101

Figure 6-11 SEM image of hemoglobin after carbonaztion procees no TCA or MS ..... 101

Figure 6-12 SEM image of the Ti3+-TiO2.................................................................................. 102

Figure 6-13 SEM image of the Ti3+-TiO2.................................................................................. 102

Figure 6-14 SEM image of the Ti3+-TiO2.................................................................................. 103

Figure 6-15 SEM image of AEM@GeZnS.......................................................................... 103

Figure 6-16 EDX of AEM@GeZnS ...................................................................................... 104

Figure 6-17 EDX of Au@GeZn............................................................................................... 104
Chapter 1

An overview of functional materials for energy-related applications

1.2 Photocatalyst for hydrogen generation

Energy demand for human beings is soaring over time. However, the primary energy source is still fossil fuels, including petroleum, coal and natural gas that comprise 86.4% of all energy consumption in the world.\(^1\) This heavy dependency on fossil fuels gives rise to two critical problems. On the one hand, fossil fuels will be depleted in the near future. On the other hand, the release of greenhouse gas CO\(_2\) generated by the combustion of fossil fuels imposes a great impact on the environment. Hydrogen gas is broadly viewed as a sustainable and clean energy alternative to the widely used fossil-based energy. As the enthalpy of H\(_2\) is as high as 286 kJ/mol and the only product after burning is water, it is an ideal energy resource.\(^2\)

Figure 1-1 Photocatalyst for hydrogen generation.
Solar energy has been considered an abundant and reliable energy source. The solar energy reaching the earth in one year is much greater than the energy that has been obtained from fossil fuels since they became an energy source over 150 years ago. Fujishima and Honda first discovered the photocatalytic splitting of water through single crystalline TiO$_2$ electrodes in 1972. Since then, a new epoch began in the heterogeneous photocatalysis for solar energy conversion and more than 100 photocatalysts have been reported. In this artificial photosynthesis process, the chemical reaction is simple:

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2+ \text{H}_2. \]

Nature’s “hydrogen economy” revolves around the hydrogenases (H$_2$ases), a class of metalloenzymes that catalyze the interconversion of protons and electrons with hydrogen. Hydrogen is both a fuel and waste product in nature. Some lithotrophic organisms obtain chemical energy through anaerobic reaction, using hydrogen as a reductant in the conversion of sulfur to H$_2$S, CO$_2$ to CH$_4$, etc.

Some photolithotrophs generate energy through photosynthetic electron transport phosphorylation, which uses hydrogen as a source of electrons. Hydrogen is produced by fermentative bacteria as a sink for reducing equivalents (i.e. electrons) and is consumed by a variety of bacteria as a source of reducing equivalents. In aerobic environments, O$_2$ is used to oxidize H$_2$ to generate water, and energy released in this process is conserved in the oxidative phosphorylation of ADP to ATP.

\[ \text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^- \]
Among the well-known H$_2$ases ([Fe]-H$_2$ase, [NiFe]-H$_2$ase, and [FeFe]-H$_2$ase) [FeFe]-H$_2$ase is the most efficient in reducing protons to molecular hydrogen (6000-9000 H$_2$ molecules per second per site).\(^9\) Several biomimetic [Fe$_2$S$_2$] complexes covalently linked to ruthenium or porphyrin photosensitizers, as light-driven H$_2$-evolving systems, have been investigated.\(^10\) The biomimetic catalysts show promising activity toward hydrogen generation, however they are limited by low stability.\(^11\)

![Figure 1-2](image)

Figure 1-2 Several biomimetic [Fe$_2$S$_2$] complexes linked porphyrin as photosensitizers.

Recently, biomimetic [Fe$_2$S$_2$] catalytic systems for hydrogen evolution driven by visible light have attracted great attention. A novel photocatalytic MOF material [FeFe](dcbdt)(CO)$_6$, (dcbdt = 1,4-dicarboxylbenzene-2,3-dithiolate) has been reported.\(^12\) The light absorption was achieved by incorporating [Ru(bpy)$_3$]$^{2+}$ in the reaction solution. The material showed greatly improved photocatalytic activity and stability for hydrogen evolution, which is a significant step forward in addressing a common issue in the development of the biomimetic catalytic system.\(^13\)
1.2 Fuel cell

The need to provide alternative energy technologies for many future generations to live comfortably is very important. Several alternative forms of technology, some proving to be more efficient and most proving to emit less greenhouse gases have been proposed. These include the use of photovoltaic (or solar) cells, which harness the sun’s energy, and convert it to electricity, and geothermal energy, which takes advantage of the thermal energy, stored deep in the earth’s crust. Hydroelectric, nuclear and wind-powered energy resources have also garnered some interest over the years. Still in more recent times, biofuels and fuel cells feature most prominently in the scientific and political discourse. Thus there are several forms of alternative energy technologies that have been proposed. However, among all of the forms of alternative energy technologies mentioned above, fuel cells offer one of the best alternatives by virtue of their high efficiency, minimal greenhouse gas emission and long term deployment.

A fuel cell is an electrochemical conversion device that converts chemical free energy to electricity without the limitation of the Carnot efficiency. In contrast to a battery, a fuel cell is an open operating system which produces electricity from externally supplied fuel and oxidants.\(^{14}\)

In the 150-year history of fuel cells, various types of fuel cells have been developed. Generally, fuel cells are characterized by the type of electrolyte: solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), and alkaline
fuel cell (AFC). The conducting ions for SOFC, MCFC and AFC are anions, formed on the cathode and transported toward the anode. On the other hand, in PEMFC, DMFC and PAFC, proton (H⁺) is the conducting species transported through the electrolyte from the anode to the cathode and the H⁺ conductivity strongly depends on the water activity. Perry and Fuller present an excellent review on the significant development of fuel cells in the past century, summarizing the applications, advantages and disadvantages of each type of fuel cell. Cost and durability are the two major hurdles for all fuel cells.¹⁵ᵃ

![Fuel cell scheme](image)

**Figure 1-3 Fuel cell scheme.¹⁵ᵇ**

The H₂-powered PEM fuel cell is perceived as an alternative to a conventional internal combustion engine for automotive applications, due to its fast start-up, low operating temperature, high fuel efficiency, and environmentally friendly advantages.¹⁶

Recently, several auto makers have introduced H₂-fed fuel cell vehicles on the road. However, some concerns—i.e., catalysts’ and membranes’ cost and durability, catalyst
activity, membrane proton conductivity, and water management—still exist. In order to make the fuel cell vehicle affordable and durable, further work needs to be done to mitigate each of the above-mentioned concerns.

Recent studies have focused on a broad range of alternative catalysts based on nonprecious metals (Fe, Co, Ni, etc.) as well as nitrogen-coordinated metal species on nanostructured catalyst supports. However, metal catalysts frequently suffer from dissolution, sintering, and agglomeration during operation of the fuel cell, which can result in catalyst degradation. To overcome this obstacle, extensive efforts have been devoted to reducing the amounts of metal species in the catalysts or replacing them with non-metal catalysts and substrates.

2.3 Photoreduction of CO\textsubscript{2}

Fossil fuels meet the majority of the global energy demand and at the same time plays a primary role in global warming. According to the Department of Energy (DOE), carbon dioxide emissions constitute 84 percent of United State greenhouse gas emissions. As with public health, there are multiple pathways in which greenhouse-gas air pollution and resultant climate change affect climate-sensitive sectors. These sectors include food production and agriculture; forestry; water resources; sea level rise and coastal areas; energy, infrastructure, and settlements; and ecosystems and wildlife. Impacts also arise from climate change occurring outside of the United States, such as national security concerns for the United States that may arise as a result of climate change impacts in other regions of the world.
In order to ensure healthy air and a stable climate for our children and grandchildren, we must make responsible decisions about our energy sources. Existing technologies and forward-thinking policies could offer practical solutions to reduce our dependence on fossil fuels. One of the solutions is to regenerate fuel from CO$_2$ by using solar energy. A critical challenge in the sustainable use of fuels is the ultimate fate of the generated CO$_2$. While photosynthesis can use solar energy to convert CO$_2$ into fuels, using only photosynthesis to recycle all anthropogenic CO$_2$ would be challenging based on natural efficiency limits and logistics.$^{23}$ Artificial photocatalytic conversion is therefore an attractive alternative to natural photosynthesis or sequestration. The US DOE has made CO$_2$ a “grand challenge” in new catalyst development.$^{22}$

Figure 1-4 Photoreduction of CO$_2$
TiO$_2$, the first reported photocatalyst, is also one of most investigated photocatalysts, due to its nontoxicity, high efficiency, easy availability, environmental benignity, and low cost.$^{24}$ Many methods—including hydrothermal, solvothermal, sol-gel, chemical vapor deposition, physical vapor deposition, microwave, and sonochemical—have been applied to prepare TiO$_2$ with various phases and shapes. It has been demonstrated that the photocatalytic activity of TiO$_2$ strongly depends on its phase structure, crystal size, specific surface area, crystallinity, and pore structure.$^{25}$

Photocatalytic reduction of CO$_2$ could be carried out in a CO$_2$-saturated aqueous solution containing suspended TiO$_2$, or in a high pressure CO$_2$ system with TiO$_2$ powders suspended in isopropyl alcohol, or in the gas phase, which would use CO$_2$ and H$_2$O vapor irradiated over TiO$_2$. In the final option, the gas phase, the UV-irradiated TiO$_2$ surface can generate electrons to reduce the CO$_2$ molecules present in aqueous and gaseous streams at ambient temperature and pressure conditions. Photogenerated electron-hole pairs migrate to the surface and in the presence of H$_2$O molecules lead to the reduction of CO$_2$ in CH$_4$.$^{26}$
1.4 References


22. Renewable Energy Sources in the United States article “nationalatlas.gov”**2011**;


Chapter 2

Incorporation of Iron Hydrogenase Active-Site into Highly Stable Metal–Organic Framework to Enhance Hydrogen Generation

2.1 Introduction

The desire for sustainable energy supply and for reducing pollution generation and global warming are primary reasons motivating scientists to study alternative energy technologies. Hydrogen (H\(_2\)) can be an ideal candidate for replacing fossil fuel dependence. Hydrogen possesses of high specific enthalpy of combustion, it also produces benign combustion products (i.e. water).\(^1,2\) In nature, enzymes named (H\(_2\)ases) use a photosynthetic complex to capture sunlight and converts its energy into H\(_2\).\(^3,4\)

Photosynthesis occurs through three primary phases. First, light is captured via absorption by chlorophyll. Next, an electron transfer occurs and lastly, the enzyme catalyzes the splitting of water into O\(_2\) and H\(_2\).\(^5\) (Figure 1)

![Figure 2-1. H\(_2\) production by using sunlight and [FeFe]-H\(_2\)ase. Reprinted with permission from ref 5 Copyright 2012 American Chemical Society](image)

Copyright 2012 American Chemical Society
Among the well-known H$_2$ases ([Fe]-H$_2$ase, [NiFe]-H$_2$ase, and [FeFe]-H$_2$ase) [FeFe]-H$_2$ase are the most efficient one in reducing protons to molecular hydrogen (6000-9000 molecules H$_2$ per second per site).$^6$ Several biomimetic [Fe$_2$S$_2$] complexes covalently linked to ruthenium or porphyrin photosensitizers, as light-driven H$_2$-evolving systems, have been investigated.$^5,7,8$ The biomimetic catalysts show promising activity towards hydrogen generation, however they are limited by low stability.$^9,10$

Metal-Organic Frameworks (MOFs) are a class of 3D porous materials constructed from metal ions covalently linked to organic linkers.$^{11-13}$ MOFs have prodigious porosity and a wide range of potential uses including drug delivery,$^{14}$ imaging,$^{15,16}$ gas storage,$^{17}$ separations$^{18}$ and catalysis.$^{19}$ By introducing catalytic active sites into MOFs, heterogeneous catalysts can be created that could foster a wide spectrum of chemical reactions.$^{19}$ Heterogeneous catalysis offers a number of advantages such as efficient recycling, ease of separation and enhanced stability.$^{20-23}$ In the sense of light-to-fuel conversion theme, photocatalyst MOF’s must efficiently collect sunlight and transport energy to catalytic center for solar fuel production.$^{24}$ Indeed, the early publication has shown rapid, efficient electron migration and long distance transfer in isomorphous MOFs.$^{24}$ Various studies have demonstrated that MOFs can be uses as platforms to integrate different molecular functional components in allowing light harvesting, photocatalytic hydrogen evolution, CO$_2$ reduction and catalysis of organic reactions.$^{25-27}$

Two common strategies have been employed for the synthesis of photocatalytically active MOFs. One method is the incorporation of organic light harvesting units, such as
2-aminoterephthalate\textsuperscript{26} and porphyrins\textsuperscript{27} into MOFs. The porous MOF with formula of \( \text{H}_2\text{TCPP}[\text{AlO}H]_2(\text{DMF}_3(\text{H}_2\text{O})_2) \) ( \( \text{H}_2\text{TCPP} \), free-basemoso-tetra(4-carboxyl-phenyl)porphyrin) that is capable of visible-light driven proton reduction at present of Pt nanoparticle, has been reported\textsuperscript{27} Another method is doping MOF with light-absorbing organometallic complexes. For example Iridium and Rhenium complexes have been incorporated into MOFs and highly active photocatalytic MOF materials have been generated\textsuperscript{28,29} The bifunctional Pt-MOF has also been successfully synthesized and the material can act as photocatalyst for the production of hydrogen\textsuperscript{30} (Figure 2)

![Figure 2-2](image_url)

**Figure 2-2.** Model structure of MOF-Pt, through post-synthetic modification of MOF with PtCl\textsubscript{2}\textsuperscript{30}

Recently biomimetic \([\text{Fe}_2\text{S}_2]\) catalytic systems for hydrogen evolution driven by visible light absorption have attracted great attention. With \([\text{Ru(bpy)}_3]^{2+}\) as a photosensitizer and \([\text{Fe}_2\text{S}_2]\) as reactive center, a novel MOF material [FeFe](dcbdt)(CO)\textsubscript{6}, (dcbdt = 1,4-dicarboxylbenzene-2,3-dithiolate) has been reported. The material showed much improved photocatalytic activity and stability for hydrogen evolution\textsuperscript{31} A common issue for the development of biomimetic catalytic system is to enhance both the photocatalytic
activity and stability. We speculate that a more stable bifunctional photocatalyst could be generated from porphyrin-based MOFs and biomimetic [Fe$_2$S$_2$] catalyst (complex 1). By coordinating biomimetics [Fe$_2$S$_2$] directly with porphyrins based MOF, a new material acting as both photosensitizer and hydrogen-evolution catalysts could be generated.

Herein, we report a catalytic system based on an organometallic Fe$_2$ complex of 1 [(i-SCH$_2$)$_2$NC(O)C$_6$H$_4$N]-Fe$_2$(CO)$_6$] and zirconium-porphyrin MOF (ZrPF). (Figure 3) Incorporation of the less stable biomimetic [Fe$_2$S$_2$] complex 1 into this highly stable zirconium based MOF could result a molecular catalyst with a high stability. The system could facilitate electron transfer due to the possibility of covalently binding of the complex 1 with photosensitizer tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCPP) that is the building unit of ZrPF thus avoiding the necessity of using electron mediator to transfer electrons from photosensitizers to the catalyst.32

![Figure 2-3. a) Model structure of biomimetic [Fe$_2$S$_2$] complex 1 and b) Model structure of zirconium-porphyrin MOF (ZrPF). Color scheme: Zr drack green, Zn orange, C gray, O red, N blue, Fe green, S yellow.](image)
2.2 Experimental section

2.2.1 Chemicals and Instrumentation

Pyrrole, elemental sulfur, propionic acid, N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), benzoic acid, acetone, iron pentacarbonyl and zinc (II) chloride, zirconyl chloride octahydrate have been purchased from Sigma-Aldrich. Powder X-ray diffraction data (XRD) were collected using a Bruker D8-Advance powder diffractometer operating at 40kV, 40mA for Cu Kα radiation (λ=1.5406 Å). The scanning electron microscopy (SEM) images were obtained on Philips XL30 FEG with the accelerating voltage at 10 kv. The sorption isotherms of N₂ were measured by using a Micromeritics ASAP 2020 surface-area and pore-size analyzer. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. Thermogravimetry analysis (TGA) was conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer. The fluorescence experiment performed at excitation wavelength of 550nm by Spex Fluorolog Tau-3 fluorescence spectrophotometer. The FTIR spectroscopy data were collected using a Nicolet 6700 FT-IR Spectrometer.

2.2.2 Synthesis of complex Fe₂S₂(CO)₆

Fe₂S₂(CO)₆ was prepared as described by Hieber and Gruber. A three neck, 5-liter round-bottomed flask was fitted with a good mechanical stirrer and a nitrogen inlet tube was flushed with nitrogen for 15 min and charged with 200 mL of methanol and 35 mL (250 mmol) of iron pentacarbonyl. The solution was cooled to 0 °C with an ice bath before 80 mL of 50% aqueous KOH (w/v) were added dropwise to the reaction over the course of 30 min. To this mixture (HFe(CO)⁴⁺) was added 83 g (2.7 mol) of elemental
sulfur, delivered in two portions over 10 min. (Caution: this step is extremely vigorous with formation of CO). The black mixture was stirred for 30 min at 0 °C, then a degassed solution of 400 ml of 50% HCl (200 mL of 37% HCl and 200 mL of distilled H₂O) were added to the reaction flask. (Cautious: acidification of the reaction mixture resulted in the evolution of H₂S). The ice bath was then removed, and the reaction mixture was stirred at room temperature for 2 h. The brown solid was collected on air, washed with 500 mL of distilled H₂O, and dried under vacuum overnight. The reaction mixture was extracted with pentane until the extracts were no longer red and this pentane extract was passed through the Celite. This solution was washed with 1000 ml of water (three washes) then dried over MgSO₄. The solvent was removed on a rotary evaporator, leaving a red-brown solid which was dried on the vacuum overnight. The red-brown solid was chromatographed on an 8 x 25-cm silica column eluting with solution of pentanes: dichloromethane (9:1). The solvent was removed, and the solid was briefly dried on the vacuum line. Sublimation of solid at 40 °C (0.1 mm) for 20 h yielded 24% red product of Fe₂S₂(CO)₆. IR (pentanes): 2084 (s), 2044 (m), 2008 (m) in the terminal CO region. Mass spectrum, m/z 344 (M⁺), 316 (M⁺ - 5CO), 176 (S₂Fe₂). We highly recommend sublimation as a method of purification.

2.2.3 Synthesis of complex [(i-SCH₂)₂NH]Fe₂(CO)₆

A red solution of S₂Fe₂(CO)₆ 0.344 g (1.0 mmol) in THF (20 mL) was cooled to -78 °C and then treated dropwise with Et₃BHLi 2.0 mL (2.0 mmol) to give a green solution containing (μ -LiS)₂Fe₂(CO)₆. After stirring for 45 min, 0.32 mL of CF₃CO₂H (2.0 mmol) was added to cause an immediate color change from green to red, indicating the
complete conversion of (μ-LiS)$_2$Fe$_2$(CO)$_6$ to (μ-HS)$_2$Fe$_2$(CO)$_6$. A mixture of 1.2 g (0.04 mol) of paraformaldehyde, 1.14 g (0.0118 mol) of (NH$_4$)$_2$CO$_3$ and 40 mL of THF was stirred for 6 h then add to a cold solution of (μ-HS)$_2$Fe$_2$(CO)$_6$. The solution allowed to warm up to room temperature after 2 hours. THF was removed under vacuum, solid was chromatographed on silica gel eluting with dichloromethane : hexane (1:8). Yield 35%.

$^1$H NMR (CD$_3$CN), 3.71 (d, 4H, NCH$_2$S), 2.22 (bm, 1H, NH) ppm. IR (hexane) 2076, 2036, 2008, 1989, 1979 cm$^{-1}$.

2.2.4 Synthesis of Complex 1[(i-SCH$_2$)$_2$NC(O)C$_6$H$_4$N]-Fe$_2$(CO)$_6$

A solution of complex [(i-SCH$_2$)$_2$NH]Fe$_2$(CO)$_6$ 0.464 g (1.2 mmol), 4-pyridine-ecarboxylic acid chloride 0.510g (3.60 mmol), and Et$_3$N 0.80 mL (5.8mmol) in CH$_2$Cl$_2$ 10 ml was stirred at room temperature for 6 h. The solution was filtrated and concentrated 1 mL under vacuum and then subjected to chromatography on silica gel eluting with petroleum ether/acetone (5/2). Yield 60% yield, IR 2078, 2039, 2002, 1680 (s) cm$^{-1}$. $^1$H NMR (300MHz, CDCl$_3$): 4.07, 4.30 (2s, 4H,), 7.34 (d, 2H), 8.77 (d, 2H).

2.2.5 Synthesis of tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCPP)

A solution of TPP-COOMe 1.69 g (2.0 mmol) and ZnCl$_2$ 3.5 g (25.6 mmol) in 150 mL of DMF was refluxed for overnight. After the mixture was cooled to room temperature, 250 mL of H$_2$O was added. The resultant precipitate was filtered and washed with 100 mL of H$_2$O for three times. The obtained solid was dissolved in Chloromethane, followed by washing two times with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative violet crystals. The obtained
ester (1.50) was stirred in THF (60 mL) and MeOH (60 mL) mixed solvent, to which a solution of KOH 5.26g (93.90 mmol) in H₂O (50 mL) was introduced. This mixture was refluxed overnight. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved, then the solution was acidified with 1M HCl. The violet solid was collected by filtration, washed with water and dried in vacuum.²¹ Yield 45%. H¹ NMR 8.80 (m, 12H), 8.39 (m, 8H), 7.81 (t, 4H) ppm.

2.2.6 Synthesis of ZrPF

A mixture of zirconyl chloride octahydrate (20.0 mg), ZnTCP, (8.0 mg), N,N-diethylformamide (DEF) (5.0 mL) and benzoic acid (200 mg) was capped in a 20 mL scintillation vials and heated at 130 °C for 3 days. Needle shaped crystals were harvested by filtration²¹ (40% yield). (Figure 2.4)

Figure 2-4. (a) tetrakis(4-carboxy-phenyl porphyrin)-zinc complex (ZnTCP). (b) The ZnTCP is connected to four 8-connected Zr₆ clusters to generated secondary building units of Zr₆O₈(CO₂)₈(H₂O)₈. (c) zirconium-prophyrin MOF (ZrPF). Color scheme: Zr drack green, Zn orange, C gray, O red, N blue, Fe green, S yellow.
2.2.7 Photocatalytic experiment

Photocatalytic H\textsubscript{2} production experiments were conducted in a sealed circulation system. In a typical run, 2 µM of [FeFe]@ZrPF (based on the catalytic di-iron subsite) suspended in buffer solution pH 5 at presence of ascorbic acid (20 mM). After degassing the system for one hour, a 300 W Xe lamp with a 420 nm cut-on filter (Newport Corp.) was applied to execute the photocatalytic reaction. The products were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). (Figure 5)

Figure 2-5. The scheme of setup for the photocatalytic water splitting.
2.3 Characterization of photocatalyst

2.3.1 High Stability of ZrPF

Zirconium-porphyrin MOF (ZrPF) was chosen as the catalyst platform since this particular MOF material exhibits high surface area, high chemical and thermal stability as well as a rigid framework structure.\textsuperscript{21} This MOF has demonstrated exceptional stability in acidic solutions (pH = 5 for 24 h) and under visible light (>420 nm) irradiation.\textsuperscript{21} The PXRD showed no framework degradation during these treatments (Figure 6). These result shows that the ZrPF is highly stable metal-organic framework (MOF).

![Figure 2-6. PXRD of ZrPF in acidic solutions (pH = 5 for 24 h) and exposure to visible light (>420 nm).](image)

1 M acetate buffer pH 5 / ZrPF after 24h

Visible light / ZrPF after 3h

ZrPF
2.3.2 Incorporation of iron hydrogenase active site into ZrPF

Pyridyl-containing Complex 1 was prepared from the treatment of the complex [(f-SCH$_2$)$_2$NH][Fe$_2$(CO)$_6$] (0.60 mmol) with isonicotinoyl chloride (1.80 mmol) in the presence of Et$_3$N (Triethylamine).$^{22}$ [FeFe]@ZrPF (complex1-ZrPF) was obtained by soaking activated ZrPF in 0.1 M solution of complex 1 in CH$_2$Cl$_2$ for 48 hours, followed by filtration and washed a few times with CH$_2$Cl$_2$. The ZrPF was decorated by complex 1 through the axial coordination of the pyridine nitrogen to the zinc porphyrin (Figure 2.7). Successful attachment of complex 1 with ZrPF was characterized by various spectroscopic methods.

![Figure 2-7. Complex 1 [(f-SCH$_2$)$_2$NC(O)C$_3$H$_4$N]-Fe$_2$(CO)$_6$. (e) [FeFe]@ZrPF (complex1- ZrPF).](image)

2.3.3 BET and XRD measurement of [FeFe]@ZrPF

The activated ZrPF exhibited a Brunauer-Emmett-Teller (BET) surface area of 836 m$^2$g$^{-1}$ measured with nitrogen at 77 K. This value is much higher than the BET surface area of [FeFe]@ZrPF (363 g/cm$^{-1}$). At single data point at relative pressure of 0.979 atm,
the total specific pore volumes of 0.482 and 0.205 cm$^3$g$^{-1}$ for ZrPF and [FeFe]@ZrPF were obtained respectively. Furthermore, a decrease in surface area is observed from N$_2$ absorption/desorption isotherms of ZrPF and [FeFe]@ZrPF (Figure 8b). The BET data support the incorporation of complex 1 with ZrPF. The simulated PXRD of ZrPF matches well with the pattern of synthesized MOF (Figure 8a). In addition, a comparison of the XRD pattern of ZrPF and [FeFe]@ZrPF showed no phase change and no framework collapse during the treatment of ZrPF with complex 1 (Figure 8a). A SEM picture demonstrated that the morphology and particle size of needle-shaped ZrPF and [FeFe]@ZrPF are almost identical.

Figure 2-8. (a) PXRD of Simulated of ZrPF, MO-ZP and [FeFe]@ZrPF. (b) N$_2$ absorption and desorption isotherms for ZrPF and [FeFe]@ZrPF.

2.3.4 Fluorescence emission of [FeFe]@ZrPF

Due to the strong fluorescence emission of ZnTCPP, according to literature, it can be an ideal sensitive probe for excited-state quenching if energy transfer or electron
transfer occurs from singlet excited state of ZnTCPP to complex 1.\textsuperscript{36,38} In our case, ZrPF shows two fluorescent emission bands at 668 and 717 nm. These were quenched after being treated with complex 1 (Figure 9). According to literature results,\textsuperscript{36,38} the observed quench is likely due to the electron transfer (ET) from the photoexcited ZnTCPP to di-Iron complex through the chemically bonded pyridine nitrogen with zinc on the axial position. These results indicate that the assembly of complex 1 and ZnTCPP through the axial position could be essential for ET.

![Normalized fluorescence spectra of ZrPF and [FeFe]@ZrPF.](image)

**Figure 2-9.** Normalized fluorescence spectra of ZrPF and [FeFe]@ZrPF.

### 2.3.5 FTIR and TGD of [FeFe]@ZrPF

Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) have been used to demonstrate the incorporation of the Fe\textsubscript{2}S\textsubscript{2} binuclear complex into the ZrPF. A characteristic feature of the hydrogenase is that the iron atoms are ligated by CO
ligands, which can be detected by FTIR spectroscopy.\textsuperscript{39} FTIR of Complex 1 exhibits three vibration bands at 2078, 2039, and 2002 cm\textsuperscript{-1} for their terminal carboxyls.\textsuperscript{36} FTIR of [FeFe]\textsubscript{2}ZrPF showed three prominent peaks from 2000 to 2100 cm\textsuperscript{-1} while no such peaks were observed for ZrPF (Figure 2.10). The TGA trace of [FeFe]\textsubscript{2}ZrPF displays two major decomposition steps at ~130-230 °C and ~380-470 °C. The partial thermal liberation of the carbonyl ligands attached to the Fe centers is the probable cause of the initial mass loss (obs: 3.4%, calcld: 3.0% based of CO lost). At ~380°C the [FeFe]\textsubscript{2}ZrPF structure starts to collapse which leads to the formation of ZnO, ZrO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} phases.\textsuperscript{31} This is in contrast to MOF-Zn, which decomposes in a single step at ~380°C.

![FTIR spectrum of ZrPF, Complex 1, and [FeFe]\textsubscript{2}ZrPF.](image)

Figure 2-10. FTIR of ZrPF, Complex 1 and [FeFe]\textsubscript{2}ZrPF.
2.3.6 ICP and EDX measurement

The extent of incorporation of the di-iron complex 1 into ZrPF was characterized by energy-dispersed X-ray spectroscopy (EDX) and inductively coupled plasma (ICP). The ratio of the elements in [FeFe]@ZrPF was determined to be 2.1:1:1 for Zn:Fe:S, normalized to Fe via EDX. This ratio suggested that ~25% incorporation of biomimetic catalyst to MOF structure based on the ratio of complex 1 to ZnTCPP (Figure 2.11). It is likely that complex 1 is integrated within the MOF, as demonstrated by the expected 1:1 Fe:S EDX ratio. The [FeFe]@ZrPF materials were digested with HF for the examination by ICP. It was found, [FeFe]@ZrPF contains ~3.8 % Fe as detected by ICP measurement, which is quite consistent with EDX data. The EDX and ICP suggested overall formula of Zr$_6$O$_8$(H$_2$O)$_8$(ZnTCPP)$_2$ [(i-SCH$_2$)$_2$NC(O)C$_3$H$_4$N]-Fe$_2$(CO)$_6$]$_{0.5}$ for [FeFe]@ZrPF.

![Figure 2-11. a) SEM and EDX analysis of ZrPF and b) SEM and EDX analysis of [FeFe]@ZrPF.](image)
2.4 Result and dissection of photocatalyst

We have explored the viability of [FeFe]@ZrPF as a catalyst in photochemical hydrogen generation. The photocatalytic activity of [FeFe]@ZrPF for H₂ evolution was evaluated by using 2 μM of [FeFe]@ZrPF (based on the catalytic di-iron subsite) in the presence of ascorbic acid, (20mM) as a sacrificial electron donor in water at pH 5 (1.0 M acetate buffer solution) under visible-light irradiation (> 420 nm). Under these reaction conditions, hydrogen production is observed and can be quantified with GC analysis. Control experiments showed no H₂ was detected when the same experiment was carried out in the absence of [FeFe]@ZrPF or sacrificial agent. Furthermore, trace amount of hydrogen was detected when just complex 1 or ZrPF was used. Also, no H₂ was observed in the dark, suggesting the photocatalytic nature of the reaction. Generally, three components are necessary for a photochemical system to drive photo-H₂ evolution: photosensitizer, proton reduction catalyst, and sacrificial electron donor, which in our system are ZnTCPP, [Fe₂S₂], and ascorbate, respectively. The ZnTCPP harvests visible light to generate ZnTCTP excited-states. Electron transfer (ET) and energy transfer to the di-iron site of complex 1 are both possible, due to the high-lying (2.06 eV) and relatively long-lived singlet excited state of ZnTCPP (ZnTCPP₁⁺), however for molecular hydrogen production only the ET pathway is needed. It is thermodynamically feasible for the direct ET from (ZnTCPP₁⁺) to complex 1 based on the reduction potential of ZnTPP₁⁺ (-1.45 V vs SCE) and the first reduction potential of [Fe₂S₂] complexes (ca. -1.20 V vs SCE). By driving an electron from ZnTCPP₁⁺ to the [Fe₂S₂] catalytic center, ZnTCPP⁺⁺ and
[Fe$^{1+}$Fe$^{0}$] species are formed. The ZnTCPP can be regenerated through reducing of ZnTCPP$^{-}$ by the sacrificial agent. It is thermodynamically unfeasible for the process of ET from ZnTCPP$^{1+}$ to [Fe$^{1+}$Fe$^{0}$] given the reduction potential of ZnTPP$^{1+}$ (-1.45 V vs SCE) and the second reduction potential of complex 1 (-1.8 V vs SCE). Therefore, [Fe$^{1+}$Fe$^{0}$] should have been protonated first in order to give the intermediate [Fe$^{1+}$Fe$^{II}$-H], which renders its reduction potential sufficiently positive for the second ET to occur. Further protonation of the intermediate [Fe$^{1+}$Fe$^{II}$-H] is followed by H$_2$ release and regeneration of complex 1.

![Figure 2-12](image.png)

**Figure 2-12.** Photocatalytic hydrogen production in the presence of [FeFe]@ZrPF (black trace, ~2 μM), complex 1 (red, ~2 μM), ZrPF (blue). Reaction condition pH 5 (1.0 M acetate buffer solution), Visible light (> 420 nm) and 20 Mmol ascorbic acid.

The dependence of hydrogen formation with irradiation time (curve in Figure 12) shows that hydrogen production rate increases almost linearly for the first 50 minutes then slows down and reaches a plateau at about 120 min. Under the aforementioned reaction conditions, after illuminating for 120 min, ~3.5 μmol H$_2$ was detected which
accounts for a turnover number of ~0.88. The turnover number and the amount of hydrogen produced by the heterogeneous catalysis of [FeFe]@ZrPF are higher than that of the corresponding homogeneous catalysts. The rate of hydrogen generation dramatically decreased after ~40 min on similar photoreaction conditions for homogeneous system. This demonstrated the higher activity and stability of the molecule catalyst inside the inorganic framework. As shown in a recent study, heterogeneous ET rate constant $k_{\text{ET,het}}$ is not higher than that of the corresponding $k_{\text{ET,hom}}$ in the similar homogeneous system. Also the photosensitizer and proton reduction catalyst, on both systems, are quite similar thus proving the reasons for the high-performance of [FeFe]@ZrPF may be caused by the enhanced stability compared to that of homogeneous system. The FTIR spectroscopic investigation of the homogenous catalyst showed that all di-iron catalyst had decomposed during the first 40 min of the reaction, since all absorptions in the CO region (2000-2100 cm$^{-1}$) of the IR spectrum had vanished. The FTIR of the heterogonous catalyst indicates that [FeFe]@ZrPF, after 40 min exposure to visible light, still shows the characteristic CO bands which is in stark contrast to the similar homogenous catalysts.

2.5 Conclusion
We have described an approach to obtain the first MOF based photocatalyst that contains both a photosensitizer and a binuclear photocatalytic H$_2$ evolution active species. Incorporation of di-iron complex 1 to ZrPF has been confirmed by BET, FTIR and other methods. Fluorescence spectroscopic results demonstrated the possible assembly of complex 1 with ZnTCPP through chemical bond on the axial position. The chemical
binding of the complex 1 to ZnTCPP could provide robust hydrogen photo-evolution systems by avoiding the necessity of using electron mediator to transfer electrons from photosensitizers to the catalyst. Due to the stabilization of the di-iron catalyst inside the highly stable inorganic framework, the heterogeneous [FeFe]@ZrPF exhibits high efficiency for photochemical hydrogen evolution in comparison with similar molecule catalysts in terms of rate and total hydrogen production yield.

Figure 2-13. H₂ production by using sunlight and [FeFe]@ZrPF.
2.6 References


42. Balzani, V.; Bergamini, G.; Marchioni, F.; Ceroni, P. Coordination Chemistry Reviews 2006, 250, 1254-1266.
Chapter 3

From Hemoglobin to Porous N-S-Fe-Doped Carbon for Efficient Oxygen Electroreduction

3.1 Introduction

Renewable energy sources are attracting growing attention for fulfilling future energy requirements, since global warming is becoming a major problem worldwide. The fuel cell, as a clean, efficient substitute for conventional energy systems, has quickly become a promising source of alternative energy.\(^1\) (Figure 3.1) Decreasing the cost per kilowatt of electric power output while improving durability and power density is a major challenge in the development of fuel cells. Currently Pt-based electrocatalysts are used for oxygen reduction reactions, but Pt is expensive. In addition, Pt-based electrodes can form stable Pt–O and Pt–OH species, which can limit the energy conversion efficiency and slow the ORR.\(^2\)

![Figure 3-1 Alkali fuel cells operate on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte.](image)

Figure 3-1 Alkali fuel cells operate on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte.
Recent studies have focused on a broad range of alternative catalysts based on nonprecious metals (Fe, Co, Ni, etc.) as well as nitrogen-coordinated metal species on nanostructured catalyst supports. However, metal catalysts frequently suffer from dissolution, sintering, and agglomeration during operation of the fuel cell, which can result in catalyst degradation. To overcome this obstacle, extensive efforts have been devoted to reducing the amounts of metal species in the catalysts or replacing them with non-metal catalysts and substrates.

Despite great progress in developing noble-metal-free catalysts, the current ORR catalysts are still far from satisfactory for large-scale practical applications. Among these developed electrocatalytic materials, carbon based oxygen reduction catalysts represent a family of promising candidates for fuel cell applications. Recently, Maruyama et al. reported the formation of noble-metal-free cathode catalysts by carbonizing hemoglobin and phthalocyanine (FePc). Additionally, they noted that porous carbonaceous materials
from hemoglobin showed great practical potential as oxygen reduction catalysts for PEFC, and abundant sources of natural hemoglobin can meet cost requirements for large scale fuel cell application. About 2.5 million tons of hemoglobin are discarded as meat waste around the world every year. Despite this low cost, the carbonized hemoglobin catalysts have low activity and durability, which limit its potential use as a replacement for conventional Pt-based catalysts.\textsuperscript{6a-b} Recently, an efficient non-precious-metal oxygen reduction reaction (ORR) catalyst from pyrolysis of an iron-coordinated complex with nitrogen rich ligand, 11,11’-bis(dipyrido[3,2-a:2′,3′-c]phenazinyl) (bidppz), has been developed. (Figure 3.3) Two active sites in the M-N/C ORR catalysts have been proposed.\textsuperscript{7} One is the M-N\textsubscript{x} species and the other is the non-metal-heteroatom doping in carbon matrix.\textsuperscript{7} Although the M-N/C catalyst shows good stability and catalytic activity, it is still lower than that of the Pt catalyst. The low surface density of catalytic sites might be one of the reasons for the lower catalytic activity.\textsuperscript{1a,2}

Figure 3-3 The ORR catalyst from pyrolysis of an iron-coordinated complex with nitrogen rich ligand. Reprinted with permission from ref 7 Copyright 2014 American Chemical Society
Hence, we report the synthesis of nitrogen-sulfur-iron-doped porous carbon materials (Fe/N/S-C-4) made by annealing hemoglobin, thiocarbamide (TCA) in the presence of mesoporous silica foam (MS) as a template in an argon atmosphere. The electrocatalytic tests show that the materials exhibited better catalytic activity and long-term stability, and higher current density and resistance than a commercial Pt/C in alkaline media for ORRs. Such excellent performance may be attributed to more accessible active sites of Fe-N₄ as well as high concentrations of dual-doping heteroatoms (N and S) that could increase the catalytic activity perhaps due to induced charge distribution on the materials.¹ᵃ, ³ᵇ

3.2 Experimental section

3.2.1 Chemicals and instrumentation

Hemoglobin from bovine blood, and thiocarbamide (Thiourea, TCA) were purchased from Sigma-Aldrich. A commercially available catalyst of 20 wt% Pt/C catalysts from Alfa Aesar was used as the conventional Pt-based catalyst. The silica oxide mesoporous (MS) also was purchased from Alfa Aesar. The 5 wt% Nafion-isopropanol solution was purchased from Ion Power. X-ray diffraction patterns (XRD) were recorded on a D8 advance diffractometer (Bruker AXS, Germany) with CuKα radiation. Transmission electron microscope (TEM) images were obtained on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. N₂ adsorption-desorption measurements were carried out at 77 K on a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra DLD using C 1s
(284.8 eV) as a reference to correct the binding energy. A Hitachi ST-4800 scanning electron microscope (SEM) was used to determine the morphology.

### 3.2.2 Synthesis catalysts

Mixtures of dry powder hemoglobin (400 mg), TCA (1600 mg) and MS (1000 mg) were finely ground together, then heated up to 1000 °C for 2 hours in a quartz tube furnace under a high purity argon atmosphere. The resultant carbon-silica composite was treated with diluted HF (10wt.%, Aldrich) solution to remove the silica template. The template-free carbon was filtered, washed with water and methanol several times, and dried in a vacuum at room temperature to give Fe/N/S-C-4. Then, by varying the TCA/hemoglobin ratios in the precursor mixtures with 0, 2:1 and 6:1, and using the same procedure as described above, three samples named Fe/N/S-C-0, Fe/N/S-C-2 and Fe/N/S-C-6 were obtained respectively. The XRD data proved that the formed materials are graphite phase carbon.7

<table>
<thead>
<tr>
<th>Samples</th>
<th>Annealing Temperature (°C)</th>
<th>Hemoglobin (mg)</th>
<th>TCA (mg)</th>
<th>MS (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/N/S-C-0</td>
<td>1000</td>
<td>400</td>
<td>0</td>
<td>200</td>
</tr>
<tr>
<td>Fe/N/S-C-2</td>
<td>1000</td>
<td>400</td>
<td>800</td>
<td>600</td>
</tr>
<tr>
<td>Fe/N/S-C-4</td>
<td>1000</td>
<td>400</td>
<td>1600</td>
<td>1000</td>
</tr>
<tr>
<td>Fe/N/S-C-6</td>
<td>1000</td>
<td>400</td>
<td>2400</td>
<td>1400</td>
</tr>
</tbody>
</table>
3.2.3 Electrochemistry experiment

The electrocatalytic activities for ORR of the as-prepared catalysts were evaluated by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on a CHI-650 electrochemical analyzer. A three-electrode cell was employed using a glass carbon RDE (5mm in diameter, Pine). One served as a working electrode, one served as an Ag/AgCl, KCl (3 M) electrode as the reference electrode, and the final was a Pt wire electrode, serving as the counter electrode. The ORR experiments were carried out in 0.1 M KOH solution. The potential was scanned at the ambient temperature between -1.2 and +0.1 V (vs Ag/AgCl) at a scan rate of 10 mV s\(^{-1}\) after purging O\(_2\) or Ar gas for 20 min. All the working electrodes were prepared as following: 10 mg catalysts were dispersed in a solution containing 1.2 mL ethanol and 0.08 mL 5 wt% Nafion-isopropanol solution, and then ultra-sonicated for 30 min. The prepared catalyst ink was pipetted onto a polished, glassy carbon electrode surface (0.196 cm\(^2\)), and the electrode was dried at room temperature. The catalyst loading of active Pt-free catalysts on the working electrode is 0.2 mg cm\(^{-2}\) in 0.1 M KOH solution. All the potentials were calibrated to the potentials vs RHE (Potentials vs RHE= potential vs Ag/AgCl +0.949 V).

3.2.4 Koutecky-Levich experiment

To further study the ORR electrochemical procedures of Fe/N/S-C-4, we performed rotating-disk electrode (RDE). The RDE current-potential curved at various rotating speeds. Therefore, the limited diffusion currents are dependent on the rate of rotation
speed. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:

\[ (1) \quad J^{-1} = J_L^{-1} + J_K^{-1} = (B \omega^{1/2})^{-1} + J_K^{-1} \]

\[ (2) \quad B = 0.62 n F C_0 (D_0^{2/3} \nu^{-1/6} \omega^{1/2}) \]

\[ (3) \quad B = n F k C_0 \]

\[ (4) \quad J_K^{-1} = J^{-1} - (0.62 n F C_0 (D_0^{2/3} \nu^{-1/6} \omega^{1/2}))^{-1} \]

Where \( J \) is the measured current density, \( J_K \) and \( J_L \) are the kinetic- and diffusion-limiting current densities, \( \omega \) is the angular velocity of the disk, \( n \) is the overall number of electrons transferred in oxygen reduction, \( F \) is the Faraday constant (\( F = 96485 \) C·mol\(^{-1}\)), \( C_0 \) is the bulk concentration of \( O_2 \) (\( C_0 = 1.2 \times 10^{-6} \) mol·cm\(^{-3}\)), \( \nu \) is the kinematic viscosity of the electrolyte (\( \nu = 0.01 \) cm\(^2\)·s\(^{-1}\)), \( D_0 \) is the diffusion coefficient of \( O_2 \) in 0.1 M KOH (\( 1.9 \times 10^{-5} \) cm\(^2\)·s\(^{-1}\)). According to Equations (1) and (2), the number of electrons transferred (\( n \)) can be calculated to be 3.80, which indicates that the FE/N/S-C-4 lead to a four-electron-transfer reaction to reduce directly oxygen into \( OH^- \).
3.3 Characterization of ORR catalysts

3.3.1 SEM and TEM images

Scanning electron microscopy (SEM) shows that the Fe/N/S-C-4 possesses uniform pore distribution. The transmission electron microscopy (TEM) image of Fe/N/S-C-4 exhibits both mesoporous and macroporous structural features. (Figure 2.5 a and.b) The morphologies of Fe/N/S-C-4 are shown in Fig 3.5.a and b, which has sponge-like structural feature with continuous 3D networks.
The elemental analysis from the EDX confirmed the presence of N, S, O, C and a small amount of Fe in the Fe/N/S-C-4. The uniform distribution of heteroatoms and Fe in the Fe/N/S-C-4 was verified by SEM-EDS and the corresponding elemental mapping images. (Figure 3.6)
3.3.2 The surface area and pore size of Fe/N/S-C-4

The surface area and pore size of the prepared materials were determined by the Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods respectively. The surface area of Fe/N/S-C-0 was 655 m$^2$ g$^{-1}$ (Fig 3.7). In the absence of MS, which has high surface area (over 800 m$^2$ g$^{-1}$), the prepared material showed a surface area of BET 60 m$^2$ g$^{-1}$. These results indicate that the MS plays a crucial role in enhancing the surface area of the materials. The N$_2$ adsorption–desorption isotherms indicated that the pore size increases with increasing mass of TCA. Furthermore, the surface area measurements show that the BET surface area increased from 655 to 737 to 1026 m$^2$ g$^{-1}$ for Fe/N/S-C-0, Fe/N/S-C-2, and Fe/N/S-C-4, respectively. (Figure 3.7) When the mass ratio of hemoglobin to TCA reached 1:6, as in the case of Fe/N/S-C-6, the surface area decreased to 850 m$^2$ g$^{-1}$, perhaps caused by the extensive TCA pyrogenation. These observations show that the mass ratios of hemoglobin to TCA play an important role in controlling the surface area of the Fe/N/S-C products.

![Adsorption–desorption isotherm of Fe/N/S-C-0, Fe/N/S-C-2 and Fe/N/S-C-4.](image)

Figure 3-7 Adsorption–desorption isotherm of Fe/N/S-C-0, Fe/N/S-C-2 and Fe/N/S-C-4.
3.3.3 The XPS measurement of Fe/N/S-C-4

X-ray photoelectron spectroscopy (XPS) was used for further investigating the chemical status of heteroatoms in the Fe/N/S-C-4. The XPS full-spectrum showed a dominant C1s peak (~284 eV), an O1s peak (~532 eV), an N1s peak (~400 eV), two S peaks (~164 eV, 228 eV) and a weak Fe peak. (Figure 3.8a) The data indicated that N, S and Fe have been successfully doped into the carbonized hemoglobin framework. The content of N, S, O and C in the Fe/N/S-C-4 were calculated to be 4.6, 2.3, 4.1, and 88.9 at%, respectively, based on the XPS peaks. Also trace amounts of Fe (~0.1%) were found on the surface of Fe/N/S-C-4. The high-resolution spectrum of C1s can be assigned into several single peaks, corresponding to C–C, C–N, C–O, C–S, C=O and C=N bonds.⁸

The high-resolution spectrum of N1s can be divided into three peaks at 398.1 eV, 400.1 eV and 401.1 eV, which can be assigned to pyridinic N, pyrrolic N and graphitic N, respectively. A peak was also observed at 404.6 eV which refers to pyridinic N⁺-O⁻ groups.⁸⁻⁹ (Figure 3.8b) The Pyridinic N and graphitic N are dominant N-types, which play significant roles in the ORR process by contributing to the p-conjugated carbonized hemoglobin with a pair of p-electrons.

The XPS-S2p spectrum also suggested the presence of \(-\text{C–S–C–} 2p_{3/2} (163.0 \text{ eV}), \text{–C–S–C–} 2p_{1/2} (164.9 \text{ eV}), \text{ and } \text{C–SO}_x\text{–C, } x = 1, 2, 3 (168.0-169.0 \text{ eV}) \) peaks. (Figure 3.9a) Data from Figure 2.9 b clearly showed the presence of two distinct forms of S: Sulfide groups (–C–S–C–) and oxidized sulfur groups (–C–SO_x–C–, x = 1, 2, 3). The XPS data showed no change in the S signal before and after sonication, supporting that the S elements are covalently bonded in the bulk of the materials and not on the surface.

3-9 The high-resolution a) C1s and b) S2p of Fe/N/S-C-4.
3.4 Electrocatalytic activity of Fe/N/S-C’s

3.4.1 Cyclic voltammetry (CV) measurement

We performed rotating disk electrode (RDE) voltammograms to investigate the electrocatalytic activity of the series of Fe/N/S-Cs for ORR in 0.1 M KOH electrolyte (Fig 3.10). When the electrolyte solution was saturated with O₂, the prominent cathodic, ORR peaks in the cyclic voltammetry (CV) curves were observed, demonstrating their effective ORR activities in the alkaline medium. The Fe/N/S-C-4 CV curves, the best sample, showed a single cathodic peak at 0.87 V (vs RHE).

![Figure 3-10 CVs for various catalysts obtained under different mass ratios of sucrose to TCA.](image)
3.4.2 Linear sweep voltammetry (LSV) measurement

To gain further insight into the ORR performances of these samples, linear sweep voltammetry (LSV) measurements were performed on a RDE at a scan rate of 10 mV S⁻¹ and a rotation rate of 1600 rpm. For comparison, a commercial Pt/C (20 wt%, Alfa Aesar) catalyst was also investigated at the same conditions. The onset potential of 0.75 V (vs RHE) was observed for the Fe/N/S-C-0 electrode. After adding TCA, it can be seen in figure 2.10 a that all samples have more positive onset potential and higher current density than Fe/N/S-C-0. Additionally, Figure 3.11 a shows that the onset potential for Fe/N/S-C-4 is similar to that of the Pt/C and current density is much higher than that of the Pt/C. These results indicate that the Fe/N/S-C-4 electrode can be a promising catalyst for the ORR in an alkaline solution.

Figure 3-11 (a) LSV curves for various catalysts and a Pt/C catalyst at a rotation rate of 1600 rpm, (b) LSV curves for various rotating speeds for Fe/N/S-C-4.
3.4.3 Influence of annealing temperature on the ORR activity

As a control experiment, the influence of annealing temperature on the ORR activity of carbonized hemoglobin material was explored. Figure 3.12 shows LSV measurement curves for carbonized materials obtained at 700 °C to 1100 °C. Our observations clearly indicate that the carbonized material obtained at 1000 °C has the highest current density and most positive onset potential of all the samples. Based on our data, we speculate that the higher temperature, which is capable of restoring defects, may be one of the factors contributing to improved graphitic degree and catalytic activity.

![LSV curves at a rotation rate of 1600 rpm for various catalysts obtained under different annealing temperature.](image)

3.4.4 Influence of MS ratio on the ORR activity

For comparison, the ORR activity of carbonized hemoglobin samples with no MS as template was investigated. The LSV monument showed the onset potential dramatically decreased when carbonizing hemoglobin in the absence of MS. These results indicated
the MS plays a significant role in the ORR activity of Fe/N/S-C-4. (Figure 3.13) Furthermore, the RDE measurement was performed at various rotating speeds to determine the kinetic process of ORR over Fe/N/S-C-4. The diffusion current densities depend on the rotating rates, and the number of electron transfers (n) involved in the ORR can be calculated from the Koutecky-Levich equation. The n for Fe/N/S-C-4 is calculated to be 3.80 at -0.40 V, suggesting a four-electron-transfer reaction to reduce oxygen directly to OH⁻, similar to ORR catalyzed by a commercial Pt/C catalyst measured in the same alkaline media.¹¹

Figure 3-13. a) LSV curves for various carbon materials, Hemoglobin (Black), Hemoglobin+TCA (Red), Fe/N/S-C-0 (Blue) and Fe/N/S-C-4 (Green) on a glass carbon rotating disk electrode in O₂-saturated 0.1 M KOH, 1600 rpm. b) LSV curves for various MS ratio, black (400mg Hem/1600mg TCA/No MS), red (400mg Hem/1600mg TCA/500mg MS), blue (400mg Hem/1600mg TCA/1000mg MS) and green (400mg Hem/1600mg TCA/2000mg MS) on a glass carbon rotating disk electrode in O₂-saturated 0.1 M KOH, 1600 rpm.

3.4.5 Resistance of the Fe/N/S-C-4 to crossover effect

Resistance to crossover effect and long-term stability of the ORR catalyst are important considerations for practical application. The chronoamperometric responses to
methanol introduced into an O₂ saturated electrolyte were measured for the Fe/N/S-C-4 and Pt/C catalysts. Figure 3.14 shows that after the addition of methanol to an electrolyte solution saturated with O₂, no noticeable change was observed in the ORR current for the Fe/N/S-C-4 electrode. In contrast, the ORR current for the Pt/C electrode decreased drastically. These results indicated high ORR selectivity and good resistance to the crossover effect of Fe/N/S-C-4.

Figure 0-14 Chronoamperometric responses of Fe/N/S-C-4 and Pt/C catalyst with 3 M methanol added at around 360 s.

3.4.6 The durability of the Fe/N/S-C-4

The durability of the Fe/N/S-C-4 and Pt/C were also compared. The catalysts were held at -0.40 V for 50000 s in O₂-saturated 0.1 M KOH solution. The result showed that the chronoamperometric response for Fe/N/S-C-4 exhibited very slow attenuation, and a high relative current of 92% persisted after 50000 s. In contrast, the Pt/C electrode
exhibited a gradual decrease, with current density loss of approximately 80% after 50000 s. (Figure 3.15)

Figure 3-15 Chronoamperometric responses of Fe/N/S-C-4 and Pt/C catalyst, at -0.40 V in an O$_2$-saturated 0.1 M KOH solution.

3.5 Result and dissection

The presence of the Fe–N$_4$ active sites could be one of the important factors for high ORR performance for Fe/S/N-C-4. In addition, dual doping of heteroatoms (N and S), porous structure and high surface area may all have contributed positively to the ORR activities of the synthesized materials. The XPS results of Fe/N/S-C-4 indicated an oxidation state of II for the Fe based on the peak positions of the Fe2p$^{3/2}$ binding energy. The presence of Fe$^{2+}$ on the surface of Fe/N/S-C-4 could play a significant role in enhancing ORR activity of Fe/N/S-C-4 since Fe$^{2+}$ on the catalyst surface is required as an O$_2$ bonding site during the first step of the multistep reaction. The ORR catalytic activity of carbonized material can be further improved by introducing heteroatoms.
Table 3-2 Summary of performance of Fe/N/S-C-4 compare to other published catalysts (at 0.1 KOH at 1600 rpm).

<table>
<thead>
<tr>
<th>Author</th>
<th>Catalyst</th>
<th>Kinetic current density (mA cm(^{-2}))</th>
<th>Onset potential (V vs.RHE)</th>
<th>Number of electrons transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wu(^{21})</td>
<td>Fe(_3)O(_4)/N-GAs</td>
<td>4.5</td>
<td>~0.75</td>
<td>3.8</td>
</tr>
<tr>
<td>Jahan(^{22})</td>
<td>Graphene–Fe–Porphyrin MOF</td>
<td>5.3</td>
<td>~0.80</td>
<td>4</td>
</tr>
<tr>
<td>Liu(^{23})</td>
<td>Sulfur–nitrogen co-doped</td>
<td>~7.0</td>
<td>0.72</td>
<td>3.9</td>
</tr>
<tr>
<td>Liang(^{24})</td>
<td>Microporous nitrogen-doped carbon</td>
<td>6.0</td>
<td>0.81</td>
<td>3.8</td>
</tr>
<tr>
<td>Cheng(^{25})</td>
<td>Pt/N-3D GNs</td>
<td>~5.5</td>
<td>0.85</td>
<td>NA</td>
</tr>
<tr>
<td>Xing(^{26})</td>
<td>Nitrogen-Doped Multilayer Graphene</td>
<td>5.8</td>
<td>~0.72</td>
<td>3.7</td>
</tr>
<tr>
<td>Wang(^{27})</td>
<td>N, S co-doped graphene</td>
<td>~5.0</td>
<td>~0.75</td>
<td>3.9</td>
</tr>
<tr>
<td>Liang(^{28})</td>
<td>Porous Fe–N Decorated Hybrids</td>
<td>~5.5</td>
<td>~0.83</td>
<td>~3.9</td>
</tr>
<tr>
<td>Our catalyst</td>
<td>Fe/N/S-C-4</td>
<td>~5.8</td>
<td>~0.82</td>
<td>3.8</td>
</tr>
</tbody>
</table>
The XPS data indicates the successful co-doping of N and S on carbonized hemoglobin, resulting in N and S content of about 4.6 and 2.3, respectively. The co-doping of heteroatoms such as N and S in the carbonized hemoglobin can introduce unpaired electrons and cause high spins and local charge density, resulting in high catalytic performance of the ORR. The table 2.2 provide Summary of performance of Fe/N/S-C-4 compare to other published catalysts.

The excellent reactant transport caused by the hierarchical 3D porous structure of Fe/N/S-C-4 can be another factor in enhancing the ORR activity. The high surface area and large pore size of Fe/N/S-C-4 caused by using MS as template and pyrogenation of TCA can also play a significant role in improving ORR activity by introducing more catalytic active sites on the surface of the materials. The pore structural feature plays a critical role in enhancing the catalytic activity due to the increase in the availability of O₂ molecules for individual active sites inside the pores of the catalyst. Watanabe et al. suggested the ORR activity would decrease when overlapping of the space occurs by a decrease in the distance between the active sites. The increase in the specific surface area could avoid this interference among the active sites, and thus increasing the pore volume of carbonized hemoglobin could expand the potential reaction space and current density.

3.6 Conclusion

In summary, porous nitrogen-sulfur-iron tri-doped carbonized hemoglobin (Fe/N/S-C-4) has been formed through a convenient, economical, and scalable route. The
experimental results have demonstrated that Fe/N/S-C-4 exhibits better catalytic activity, higher current density, longer-term stability and higher methanol tolerance than the commercial 20% Pt/C catalyst. This study demonstrates that carbonized hemoglobin in the presence of MS and TCA is effective for the formation of highly porous carbon materials that show enhanced activity as the fuel cell catalyst.

Figure 3-16 The Fe/N/S-C-4 has been formed through a convenient, economical, and scalable route.
3.7 References


   (b) http://www3.imperial.ac.uk/fuelcells/research/afcdevelopment


Chapter 4

Self-doped Ti$^{3+}$-TiO$_2$ as Photocatalyst for the Reduction of CO$_2$ into Hydrocarbon Fuel under Visible Light.

4.1 Introduction

Currently, fossil fuel meets the majority of global energy demands and at the same time plays the main role in global warming. Carbon dioxide (CO$_2$) emission from fossil fuels constitutes 84 percent of worldwide green gas emissions.$^1$ Regeneration of fuel from CO$_2$ by using solar energy is a possible solution for global warming. In fact, the idea of mimicking the overall natural photosynthetic cycle of the chemical conversion of CO$_2$ into useful fuels has been studied extensively in last 30 years.$^2$ Artificial photosynthesis via photocatalysts allows the direct conversion of CO$_2$ and water into valuable hydrocarbon such as CH$_4$, CH$_3$OH and C$_2$H$_5$OH by using sunlight.$^3$ (Scheme 3.1)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0_{\text{red}}$ V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\text{H}^+ + 2e^-$</td>
<td>-0.41</td>
</tr>
<tr>
<td>$\text{H}_2$O</td>
<td>$\rightarrow$ $\frac{1}{2}\text{O}_2$ + $2\text{H}^+$ + $2e^-$</td>
</tr>
<tr>
<td>$\text{CO}_2 + e^-$</td>
<td>$\rightarrow$ $\text{CO}_2^-$</td>
</tr>
<tr>
<td>$\text{CO}_2 + \text{H}^+ + 2e^-$</td>
<td>$\rightarrow$ $\text{HCO}_3^-$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 2\text{H}^+ + 2e^-$</td>
<td>$\rightarrow$ $\text{CO} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 4\text{H}^+ + 4e^-$</td>
<td>$\rightarrow$ $\text{HCHO} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 8\text{H}^+ + 6e^-$</td>
<td>$\rightarrow$ $\text{CH}_3\text{OH} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{CO}_2 + 8\text{H}^+ + 8e^-$</td>
<td>$\rightarrow$ $\text{CH}_4 + 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

Scheme 4-1 One, two, six and eight electron reduction potentials (vs.NHE) of some reactions involved in CO$_2$ photoreduction at pH 7.

Among the present photocatalysts for CO$_2$ conversion, TiO$_2$-based semiconductors have been the most popular ones. TiO$_2$, the first reported photocatalyst, is also one of the
most investigated, due to its nontoxicity, high efficiency, easy availability, and low cost. Many methods, including sol-gel, chemical vapor deposition, solvothermal and microwave methods have been applied to prepare TiO$_2$ with various phases and shapes. It has been demonstrated that the photocatalytic activity of TiO$_2$ strongly depends on its phase structure, crystal size, specific surface area, and crystallinity. In spite of extensive studies of CO$_2$ photoreduction by TiO$_2$, the progress in this area is not as significant as hydrogen photogeneration from water, due to low efficiency of photocatalysts. The poor photoreduction of CO$_2$ is caused by several limiting factors such as fast electron-hole recombination rates, low CO$_2$ affinity to the photocatalyst, and narrow light absorption wavelength range for wide band-gap semiconductors such as TiO$_2$. In fact, pure TiO$_2$ is active under ultraviolet (UV) irradiation that is a very small proportion (about 3–5%) of solar radiation. Therefore, band-gap engineering is required to use TiO$_2$ as efficient catalytic materials. The TiO$_2$ band gap should be narrow enough to capture part of the visible light spectrum where most of the solar energy exists, and it should also match the CO$_2$ reduction potential requirements for the desired products. (Scheme 4.1)

Doping is one of the popular strategies to overcome the above limitations. The introduction of a metal such as Fe, Mn and Cr or a nonmetal such as N and S in the TiO$_2$ lattice could create additional energy states within the band gap. As a result, the white color of TiO$_2$ might change, giving a clear sign that visible light has been absorbed. However, the visible light response doesn’t necessarily improve the photocatalytic activity because the introduction of these doping materials may also introduce
recombination centres for photogenerated charges.\textsuperscript{14} Self-doping could provide a more efficient alternative to existing doping methods. For instance, a two-dimensional TiO\textsubscript{2} phase with a narrow band gap (ca. 2.1 eV) could be formed by the rearrangement of surface atoms of rutile TiO\textsubscript{2}.\textsuperscript{15} The self-doping TiO\textsubscript{2} (Ti\textsuperscript{3+}-TiO\textsubscript{2}) based photocatalytic materials were also reported for H\textsubscript{2} generation and decomposition of gaseous 2-propanol under visible light.\textsuperscript{16} Recently, we have developed facile one-step combustion and hydrothermal methods to synthesize partially reduced and self-doped TiO\textsubscript{2} (Ti\textsuperscript{3+}-TiO\textsubscript{2}), which is a highly active photocatalyst for H\textsubscript{2} generation under visible light.\textsuperscript{17}

![Solar Radiation Spectrum](image)

Figure 4-1 The solar radiation spectrum for direct light at both the top of the Earth's atmosphere and at sea level.\textsuperscript{17b}

Herein we demonstrated that these self-doped Ti\textsuperscript{3+}-TiO\textsubscript{2} could be used as visible light photocatalysts for the photoreduction of CO\textsubscript{2} to CH\textsubscript{4}. The incorporation of Ti\textsuperscript{3+} into the TiO\textsubscript{2} narrows the band gap (2.90 eV) and extends the light absorption from the UV into
the visible range. In addition, the introduction of a Cu/Pd on the surface of Ti$^{3+}$-TiO$_2$ as co-catalyst has further enhanced photocatalytic activity for the conversion of CO$_2$ to CH$_4$.

4.2 Experimental section

4.2.1 Synthesis of self-doped Ti$^{3+}$-TiO$_2$

All chemicals, including titanium powder (Aldrich, 99%) and hydrochloric acid (Fisher scientific, 37.1%), were used as received without any further purification. In a typical synthetic procedure, titanium powder (0.300 g) and hydrochloric acid (10 mL, 2M) were mixed in a 50 mL beaker and magnetically stirred for 30 min. This mixture was then transferred to the Teflon-lined stainless-steel autoclave (23 mL capacity) and hydrothermally treated for a night under 220° C. The sample was then collected and washed by distilled water and ethanol few times.$^{17a}$

4.2.2 Characterization of self-doped Ti$^{3+}$-TiO$_2$

X-ray diffraction patterns (XRD) were recorded on a D8 advance diffractometer (Bruker AXS, Germany) with CuKα radiation. Transmission electron microscope (TEM) images were obtained on a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. N2 adsorption-desorption measurements were carried out at 77 K on a Micromeritics ASAP 2020 analyzer. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Axis Ultra DLD using C 1s (284.8 eV) as a reference to correct the binding energy. A Hitachi ST-4800 scanning electron microscope (SEM) was used to determine the morphology.
4.2.3 Photoreduction of CO$_2$

Photocatalytic reduction of CO$_2$ in the presence of H$_2$O was carried out in a lab bench reactor (volume, ~400 mL) with a quartz window on the top of the reactor. The light source was a 300 W Xe lamp with a 400 nm cut-on filter (Newport Corp.). The photocatalytic reaction was performed in a gas (vapor)-solid heterogeneous reaction mode. Typically, 100 mg of solid catalyst was placed on a Teflon catalyst holder in the upper region of the reactor. Liquid water with a volume of 4 mL was pre-charged in the bottom of the reactor.

![Figure 4-2](image)

Figure 4-2 a) Photograph of the reaction chambers set in the sunlight. Reprinted with permission from ref 18a Copyright 2009 American Chemical Society b) Our designed system.

It should be noted that the catalyst was not immersed into the liquid water. Instead, the catalyst was surrounded by H$_2$O vapor and CO$_2$. The pressure of CO$_2$ was typically regulated to 1 atm. The photocatalytic reaction was typically performed for 6 h. The amounts of CH$_4$ formed were analyzed by gas chromatography. We adopted a flame
ionization detector (FID) for quantifying the amounts of CH$_4$ formed from CO$_2$ to ensure high sensitivities. Argon was used as the carrier gas. We performed the same experiment (including both reaction and detection) for at least 3 times for each catalyst, and the relative error was <5%.

### 4.2.4 Flat-band potential measurement

Mott–Schottky plots were recorded on an electrochemical workstation (CHI650E, Chenhua, Shanghai) by using the Impedance-Potential technique. The working electrode was prepared on fluorine-doped tin oxide (FTO) glasses, which was cleaned by sonication in chloroform, acetone and ethanol for 30 min, respectively. The glass was then rinsed with millipore water and kept in isopropanol (or ethanol). 5 mg ultrafine powder was mixed with 0.5 mL dimethyl formamide under sonication for 2 h to get slurry. The slurry was spreading onto FTO glass whose side part was previously protected using Scotch tape. A copper wire was connected to the side part of the FTO glass using a conductive tape. Uncoated parts of the electrode were isolated with epoxy resin, and the exposed area of the electrode was 0.25 cm$^2$.

Electrochemical measurements were performed in a conventional three electrode cell, using a Pt plate and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The working electrodes were immersed in a 0.2 M Na$_2$SO$_4$ aqueous solution (pH ~6.9) without additive for 30 s before measurement was carried out. For Mott-Schottky experiments, the potential ranged from -0.4 to 1.2 V (vs.
Ag/AgCl), and the perturbation signal were 10 mV with the frequency from 1.25 to 0.5 kHz. The potential was swept at a sweep rate of 10 mV s\(^{-1}\) or 20 mV s\(^{-1}\).\(^{18b}\)

Data treatment

\[ Cs = -1/(2\pi \times Z'' \times F) \]

where \(Cs\) is the capacitance of the self-supported film electrodes; \(Z''\) is the virtual resistance; \(F\) is the given frequency.

Mott–Schottky plot: \(1/(Cs \times Cs) \sim \text{Potential} \)

From figure 2, the flat-band potential of Ti\(^{3+}\)-TiO\(_2\) is \(~-0.65\) vs. Ag/AgCl. To convert the potential to be against the normal hydrogen electrode (NHE), +0.197 V has to be added according the following equation\(^{18b}\).

Figure 4-3  Mott-Schottky plot obtained at different frequencies for Ti\(^{3+}\)-TiO\(_2\).
E(NHE) = E(Ag/AgCl) + 0.197

Hence, the flat band potential of Ti$^{3+}$-TiO$_2$ is -0.45 vs. NHE.

4.3 Results

4.3.1 Hydrothermal reaction

In the hydrothermal condition, previous report suggested that the chemical reaction in the autoclave is as follows 17a

\[
2\text{Ti (powder)} + 6\text{H}^+ \rightarrow 2\text{Ti}^{3+} + 3\text{H}_2
\]

\[
\text{Ti}^{3+} + \text{H}_2\text{O} \rightarrow \text{TiOH}^{2+} + \text{H}^+
\]

\[
\text{TiOH}^{2+} \rightarrow e^- + \text{Ti(IV) oxo species} \rightarrow \text{TiO}_2
\]

\[
\text{TiO}_2 + \text{H}_2 \rightarrow \text{TiO}_{2-x} + \text{H}_2\text{O}
\]

4.3.2 EPR and XRD results

The powder X-ray diffraction (XRD) analysis shows that reduced TiO$_2$ with rutile phase has formed. A high resolution SEM image reveals that the rutile crystal has a pyramid-shape similar to the Ti$^{3+}$-TiO$_2$ previously reported. 17 Electron paramagnetic spectra (EPR) were recorded at low temperature (100 k) to determine the presence of Ti$^{3+}$. A strong EPR signal was observed at g=1.97, which can be assigned as Ti$^{3+}$ peak (figure 4.4c). 17

The Ti$^{3+}$ is formed as the result of reducing Ti$^{4+}$ by H$_2$, which is produced by a reaction between titanium powder and hydrochloric acid. The Ti$^{3+}$ concentrations were
estimated to be \( \approx 4.5 \, \mu \text{mol g}^{-1} \), using numerical double integration of EPR peak and comparison with a frozen aqueous solution of Cu\(^{2+}\).\(^{18c}\)

![EPR spectra and XRD patterns](image)

Figure 4-4 a) EPR spectra measured at 100 K. b) XRD patterns for the Ti\(^{3+}\)-TiO\(_2\).

4.3.3 UV/vis absorption spectra and XPS measurement

In addition, X-ray photoelectron spectroscopy (XPS) was used to study the surface elemental composition of the Ti\(^{3+}\)-TiO\(_2\) crystal. The XPS result shows the presence of the Ti 2p\(_{3/2}\) and O1s peaks. However, The XPS study shows no evidence of Ti\(^{3+}\) on the surface of the crystal. Having Ti\(^{3+}\) in the bulk of the crystal is crucial for the stability of the Ti\(^{4+}\)-TiO\(_2\) catalyst since the oxygen defects on the surface usually are not stable enough to survive in the air.\(^{19}\) (Figure 4.5)
Figure 4-5 The Ti 2p XPS spectra of the Ti$^{3+}$-TiO$_2$. No Ti$^{3+}$ signal (at 456.6 eV) was detected.

Moreover, in comparison to the commercial TiO$_2$ (P25), our Ti$^{3+}$-TiO$_2$ catalyst shows red shift in the UV/vis absorption spectra, that suggested narrowing band gap from UV range to visible light spectrum (figure 3.6).

Figure 4-6 UV/Vis diffuse reflectance spectra for commercial P25 (red) and Ti$^{3+}$-TiO$_2$ (black).
4.3.4 Co-catalyst effect

Co-catalysts are known to play significant roles in enhancing semiconductors’ photocatalytic activity. The incorporation of metals like Pt, Pd, Au, Cu, Ru and Ag on a TiO\textsubscript{2} surface can increase the activity of photoreduction of CO\textsubscript{2} in several ways such as increasing the charge separation and retarding recombination, trapping of charge carrier, and activation of CO\textsubscript{2} and H\textsubscript{2}O\textsuperscript{20}. These three factors thus could facilitate further surface transformations, leading to desired hydrocarbon products. It has also been reported that binary co-catalysts, such as Pt and Au with Cu, can increase the efficiency of the photocatalytic CO\textsubscript{2} reduction, leading mainly to the production of methane with a good selectivity\textsuperscript{21}. As such, we have introduced both Cu and Pd co-catalysts on the Ti\textsuperscript{3+}-TiO\textsubscript{2}. The stepwise photodeposition technique has been used to load Pd and Cu binary co-catalysts on the Ti\textsuperscript{3+}-TiO\textsubscript{2}.

Figure 4-7 The Pd 3d XPS spectra of the Pd/Ti\textsuperscript{3+}-TiO\textsubscript{2}. 

68
Briefly in this case, Pd nanoparticles were first introduced onto Ti\textsuperscript{3+}-TiO\textsubscript{2} by photoreducing H\textsubscript{2}PdCl\textsubscript{6} in an aqueous suspension. Then, Cu was deposited onto Pd/Ti\textsuperscript{3+}-TiO\textsubscript{2} under 4 hours of UV-vis irradiation using a CuSO\textsubscript{4} solution.\textsuperscript{21a} The chemical states of Pd and Cu in our samples were further characterized by XRD and the XPS analyses. XRD result shows that only Ti\textsuperscript{3+}-TiO\textsubscript{2} diffraction peaks were observed. The XPS measurements revealed that the binding energies at 335.1 and 340.2 eV for Pd 3d\textsubscript{5/2} and Pd 3d\textsubscript{7/2}, respectively.\textsuperscript{22} The Pd/Ti\textsuperscript{3+}-TiO\textsubscript{2} and Cu\textsuperscript{I}/Pd/ Ti\textsuperscript{3+}-TiO\textsubscript{2} samples confirmed that Pd exists as metallic state in the samples. The binding energies of Cu 2p\textsubscript{3/2} for Cu\textsuperscript{I}/Ti\textsuperscript{3+}-TiO\textsubscript{2} and Pd/Cu\textsuperscript{I}/Ti\textsuperscript{3+}-TiO\textsubscript{2} samples were about 932.5 eV, which could be contributed to the presence of Cu\textsuperscript{I} since the Cu\textsuperscript{0} could be easily oxidized into Cu\textsuperscript{I} (Cu\textsubscript{2}O).\textsuperscript{21a} (Figure 4.8)

![Intensity vs Binding Energy](image_url)

Figure 4-8 The Cu 2p XPS spectra of the Cu\textsuperscript{I}/Ti\textsuperscript{3+}-TiO\textsubscript{2} and the Cu\textsuperscript{I}/Pd/Ti\textsuperscript{3+}-TiO\textsubscript{2}.
Additionally, Figure 4.9 shows the high-resolution transmission electron microscope (HRTEM) image for the Cu/I/Pd/ Ti$^{3+}$-TiO$_2$. The observation of the co-catalysts exclusively forming on the {110} facets, not on the {111} facets confirmed that the photogenerated electrons prefer the {110} facets over {111} facets.

![TEM image of Pd@Cu/Ti$^{3+}$-TiO$_2$ nanoparticles on {111} facets]

Figure 4-9. The TEM image of a Pd@Cu/Ti$^{3+}$-TiO$_2$, nanoparticles found on the {111} facets

### 4.3.5 Photoreduction of CO$_2$ to CH$_4$

The photocatalytic activity of Ti$^{3+}$-TiO$_2$-based materials for CO$_2$ reduction into CH$_4$ was determined in the gas phase under batch conditions. A Xe lamp (300 W) with a 400 nm cut-on filter was used to cut off the UV light and allow only visible light (>400 nm) to pass through. Figure 4.10 shows that the loading of either Pd or Cu$^1$ (existing as Cu$_2$O) single co-catalysts onto Ti$^{3+}$-TiO$_2$ can promote the formation of CH$_4$. Moreover, the rate of CH$_4$ formation over Cu$^1$/Pd/ Ti$^{3+}$-TiO$_2$ catalyst was about 6.5 times higher than that
over Ti$^{3+}$-TiO$_2$ alone. For Pd/Ti$^{3+}$-TiO$_2$ and Cu$^1$/Ti$^{3+}$-TiO$_2$ catalysts, the rates of formation were 4.0 and 1.5 times higher, respectively.

![Figure 4-10](image)

**Figure 4-10** The CH$_4$ formation under different co-catalysts on Ti$^{3+}$-TiO$_2$, no co-catalyst (black), Cu$^1$ (green), Pd (brown) and Cu$^1$/Pd (blue).

To prove the photocatalytic CO$_2$ conversion, control experiments were conducted, including (I) for long periods in the presence of CO$_2$ and H$_2$O with the catalyst in the dark; (II) in the absence of photocatalyst; (III) and in the absence of CO$_2$ or H$_2$O. Analysis of the gas phase in these three controls did not lead to the detection of any reaction products. In addition, we have compared the photoreduction activity of this reported sample prepared by hydrothermal method with the sample prepared by our previously reported combustion method for reduced TiO$_2$ (Ti$^{3+}$-TiO$_2$). The Ti$^{3+}$-TiO$_2$ photocatalyst prepared here by the hydrothermal method shows about 2.5 more CH$_4$ generation than the Ti$^{3+}$-TiO$_2$ from combustion. (Figure 4.11)
Figure 4-11 The CH₄ formation under different photocatalyst, P25 (black), RC-TiO₂ (red) and Ti⁺³-TiO₂ (blue).

4.4 Discussion

The photogenerated holes in the valence band oxidize water and generate hydrogen ions through the reaction of \( \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \) \((E_{0 \text{redox}} = 0.82 \text{ V vs. NHE})\). The photogenerated electrons in the conduction band reduce CO₂ to CH₄ by the reaction of \( \text{redox CO}_2 + 4\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \) \((E_{0 \text{redox}} = -0.24 \text{ V vs. NHE})\). \(^{23}\)

Functionally, to produce hydrogen cations, the photocatalyst should have the valence band of top energy levels suitable for water splitting. The bottom energy level of the conduction band should be more negative with respect to the reduction potential of CO₂ into CH₄.

The band gaps of Ti⁺³-TiO₂ were determined to be 2.9 eV by UV-vis absorption spectra. Also the position of the flat band of Ti⁺³-TiO₂ was determined using Mott–Schottky plots. The edge of the conduction band was estimated to be -0.45 V (vs NHE), which was more negative than that.
Figure 4-12 Flat-band and conduction band of the Ti$^{3+}$-TiO$_2$.

of $E_0$ (CO$_2$/CH$_4$) (-0.24 vs NHE). Meanwhile, the edge of the valence band was determined to be 2.45 V, which was more positive than that of $E_0$ (H$_2$O/H$_2^+$) (0.82 V vs NHE). These results indicate that the photogenerated electrons and holes on irradiated Ti$^{3+}$-TiO$_2$ can react with the absorbed CO$_2$ and H$_2$O to generate CH$_4$. Figure 4.11 shows the rate formation of CH$_4$ over the prepared Ti$^{3+}$-TiO$_2$ from the hydrothermal and from combustion methods under light above 400 nm. The surface areas of the Ti$^{3+}$-TiO$_2$ prepared by hydrothermal and combustion methods were determined to be 5.0 m$^2$g$^{-1}$ and 12.3 m$^2$g$^{-1}$, respectively, which may seem counterintuitive in contrast to their photoactivity because the Ti$^{3+}$-TiO$_2$ from hydrothermal shows approximately a 2.5 times higher CH$_4$ formation than the sample prepared from combustion method. This result indicates that the higher activity of the Ti$^{3+}$-TiO$_2$ must come from other structural features such as morphology and crystal shape. In fact, it has been reported that {111} and {110} facets are prone to collect holes and electrons, which respectively improves the separation of holes and electrons (figure 4.9). Therefore, the higher photocatalytic activity of the Ti$^{3+}$-TiO$_2$ might be
Figure 4.13  N₂ adsorption-desorption isotherms of Ti³⁺-TiO₂ from hydrothermal and RC-TiO₂ from combustion method.

due to trapped electrons and holes in different crystal facets of the Ti³⁺-TiO₂, such as the {111} and {110}. The trapped electrons and holes could suppress rapid recombination that can increase the opportunities to initiate surface reactions, thus enhancing the photocatalytic activity. Moreover, additional evidence suggests doping the metals as co-catalyst can further enhance electron–hole separation, leading to higher catalytic activity. Our present work further clarified that the formation of CH₄ was also enhanced by loading Pd or Cu¹ onto Ti³⁺-TiO₂, and such an enhancement was much more significant in the case of Cu¹/Pd co-catalysts (Fig. 4.10). These results show that the rate formation of CH₄ over Pd/Ti³⁺–TiO₂ is higher than Cu¹/Ti³⁺–TiO₂. The lower photocatalytic activity of Cu¹/Ti³⁺–TiO₂ might be the result of lower efficiency of the separation of photogenerated electron–hole pairs in the Cu¹/Ti³⁺–TiO₂ catalyst. On the other hand, the Cu¹/Pd/ Ti³⁺-TiO₂ catalyst containing the Pd/Cu¹ demonstrated a significantly enhanced activity for the formation of CH₄. The Cu¹ structure may cause higher activity by
preferential activation and conversion of CO$_2$ molecules in the presence of H$_2$O, while the Pd particles effectively extracted the photogenerated electrons from Ti$^{3+}$–TiO$_2$.\textsuperscript{21}

4.5 Conclusion

In conclusion, we have studied photoreduction of CO$_2$ with a partially reduced non-stoichiometric rutile TiO$_2$ from the hydrothermal method with active facets. This highly stable photocatalytic material has a greatly improved efficiency to reduce CO$_2$ under visible light when compared to the Ti$^{3+}$-TiO$_2$ from combustion method. Additionally, our results clearly demonstrated that using the co-catalysts such as Cu$^+/Pd$ might be a potential breakthrough to further improve the photocatalytic activity for CO$_2$ reduction with H$_2$O.

Figure 4-14 Photoreduction of CO$_2$ with a partially reduced non-stoichiometric rutile TiO$_2$ with active facets.
4.6 References


Chapter 5

Metal-doped open-framework chalcogenides as efficient Photocatalysts for reduction of CO$_2$ into renewable hydrocarbon fuel

5.1 Introduction

Converting solar light to chemical energy has been an attractive research area since the first photocatalysis was reported three decades ago. Particularly, using photocatalysis for water splitting in order to produce hydrogen as a clean and recyclable source of energy has been studied extensively. Today, over 130 materials are well known as photocatalysts for water splitting.$^1$ As also reported by Fujishima and his co-workers in 1979, photoreduction of CO$_2$ using a photocatalyst such as TiO$_2$ is also possible.$^2$ In spite of the economic and environmental benefit of CO$_2$ photoreduction, the research in this area has not significantly progressed as in hydrogen production because the photoreduction of CO$_2$ pathways are very complex and always suffer from low efficiency.$^3$ Recently, however CO$_2$ photoreduction catalysis attracted a great deal of renewed attention because of rising CO$_2$ emissions, which contribute to global warming.$^4,5$

Several limiting factors, such as fast electron-hole (e$^-$ h$^+$) recombination rates, complicated backward reactions and low CO$_2$ affinity of the photocatalysts, cause the CO$_2$ photoreduction catalyst to have a low efficiency.$^6$ Also, the main challenge for
developing new photocatalysts is increasing the number of available electrons for the CO$_2$ reduction process, and the ability to use these electrons at a rate that is sufficient with the photon incident rate. For instance, if the reaction proceeds via a two electrons redox reaction, CO$_2$ is converted to carbon monoxide (CO), whereas CH$_4$ formation involves an eight electrons redox reaction. Another challenge is designing a photocatalyst with suitable band gap for CO$_2$ photoreduction. In fact, the semiconductor band gap must be narrow enough to capture part of the visible light spectrum where most of the solar energy exists, and the band edge must match the CO$_2$ reduction potential requirements for the desired products.

Figure 5-1 Photoreduction of CO$_2$ and carbon cycle.

To overcome the above stated limitations, systematic modifications of both the electronic band gap and energy level of each individual band are necessary. In addition, a photocatalyst with a large number of active sites for increasing quantum efficiency is highly favorable. Recently, we have been developing a new approach to the synthesis of highly porous chalcogenide clusters with the expectation of increased photocatalytic
activity for CO$_2$ reduction.$^{10,11}$ Such porous crystalline semiconductors can offer several unique advantages for photoreduction of CO$_2$.$^{12,13}$ One such advantage is the possibility to tune the band gap structure of the chalcogenide clusters by controlling framework architecture.$^{14}$ Another possible advantage is the crystalline porous material can offer a large number of active sites because of their high surface area.$^{15}$ Additionally, the electron-holes recombination rate is expected to decrease since unlike in dense materials, electrons and holes do not have to travel all the way to a catalyst’s surface for a reaction to occur.$^{16}$ Moreover, a large number of cavities within the open framework can serve as hosts for incorporation of noble metals, dyes, or other optically active compounds.$^{15}$ Incorporating such optically active materials are often highly desirable for improving photocatalytic efficiency.$^{16,17}$ Unfortunately, whereas a large number of open frameworks have been developed in the last decade, most of them are unsuitable for photocatalytic reactions because they are insulating oxides, have wide bandgaps, or they are prone to photocorrosion under light irradiation.$^{16}$

Figure 5-2 Three-dimensional framework of AEM@GeZnS the blue sphere represent the void inside the cage. Color scheme, S green and Ge/Zn purple.
Recently, a large family of crystalline chalcogenide open frameworks were developed. These materials have great potential to be used as efficient photocatalysts for CO$_2$ reduction since they have unique, highly porous open framework architecture with tunable band gaps as well as high thermal and light stability. In this chapter, we describe the photocatalytic properties of the selected crystalline open framework of sulfide cluster (AEM@GeZnS). We demonstrate that doping metal cations such as Au$^{3+}$, Pd$^{2+}$ to GeZnS framework can tune the band gaps, resulting in improved photocatalytic efficiency of the chalcogenide cluster. The photocatalytic materials of Au@GeZnS and Pd@GeZnS show significant improvement of the photocatalytic activity, encouraging reduction of CO$_2$ into renewable hydrocarbon fuel (CH$_4$) in the presence of water vapor.

5.2 Experimental section

5.2.1 Chemicals and instrumentation

All of the reagents used were obtained from commercial supplies without further purification. Germanium (= Ge, -100 mesh, 99.999%, Alfa Aesar), germanium (IV) oxide (= GeO$_2$, 99.999%, Acros Organics), tin powder (= Sn, -100 mesh, 99.5%, Alfa Aesar), sulfur powder (= S, -100 mesh, 99.5%, Alfa Aesar), Zn(NO$_3$)$_2$·6H$_2$O (98% extrapure, Acros Organics), N-(2-aminoethyl)-morpholine (= AEM, C$_6$H$_{14}$N$_2$O, 98+, Alfa Aesar).

Single-crystal X-ray analysis was performed on a Bruker APEX II diffractometer with nitrogen-flow temperature controller using graphite-monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$ Å), operating in the $\omega$ and $\varphi$ scan mode. The SADABS programme was used for absorption correction. The structures were solved by direct or Patterson methods.
followed by successive difference Fourier methods. All atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against $F^2$. Powder X-ray diffraction (PXRD) experiments were performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40 kV and 40 mA (CuKα radiation, $\lambda = 1.5418$ Å). The data collection was performed with a step size of 0.02° and counting time of 2 or 5 or 10 seconds per step. The simulated powder XRD pattern was obtained from the single-crystal data. The thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 apparatus in the temperature range of 30 °C to 900 °C under N₂ flow at a heating rate of 5 °C/min. Elemental Analysis (EA) was carried out with a Perkin-Elmer 2400 CHNS Elemental Analyzer (Atlantic Microlab, Inc.). Metal contents were measured by Agilent inductively coupled plasma mass spectrometer (ICP-MS) 7500cx with the autosampler (chemistry, UCR). Solid-state diffuse reflectance spectra were recorded on a Shimadzu UV-3101PC spectrophotometer, its absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function. Scanning electron microscopy (SEM) images were taken on Philips FEI XL30 field emission scanning electron microscope (FESEM) equipped with PGT-IMIX PTS energy dispersive spectroscopy (EDS) detector, or on Nova NanoSEM450 (Schottky field emmission scanning electron microscope).

5.2.2 Synthesis of AEM@GeZnS cluster

0.090 mg (1.23 mmol) of Ge (or GeO₂, 0.120 g, 1.14 mmol), 0.090 mg (0.30 mmol) of Zn(NO₃)₂·6H₂O, 0.220 g (6.88 mmol) of sulfur, and 2.5 mL of N-(2-aminoethyl)morpholine (AEM) were mixed in a 23 mL Teflon-lined stainless autoclave
and stirred for ca. 30 min. The vessel was then sealed and heated at 190 ºC for 12 days. After cooling to room temperature, 0.108 g of AEM@GeZnS crystals was obtained as large light-yellow rhombic-dodecahedral crystals.

Figure 5-3 Photographes of AEM@GeZnS. Reprinted with permission from ref 17b copyright 2015 American Chemical Society. (Photo credit: Qipu Lin).

5.2.3 Preparation of film of AEM@GeZnS deposited on FTO electrode

Typical preparation of film of AEM@GeZnS on FTO electrode: 25.0mg of ground AEM@GeZnS powder was dispersed in 50mL isopropanol with the presence of 5.0 mg of Mg(NO$_3$)$_2$·6H$_2$O. The sealed mixture suspension was continuously stirred for 2 days, and then was ultrasonically vibrated for one hour before electrophoretic deposition. The clean and sleek platinum plate electrode was used as anode, and the fluorine-doped tin-oxide (FTO) conductive glass as cathode. Constant working voltage was set up to 50V. The whole electro-deposition process lasted for 30 minutes. The obtained FTO electrode decorated with ISC-10s film on its surface was finally washed with ethanol to remove residual isopropanol and Mg(NO$_3$)$_2$ salt left in suspension.
5.2.3 Photoelectrochemical measurements

Photoelectrochemical studies on the films of ISC-10s samples on FTO substrate were performed on a Solartron SI 1287 electrochemical interface analysis instrument operated with CorrWare program in a standard three-electrode configuration 5 with a FTO electrode modified with AEM@GeZnS samples as the photoanode (an effective area is ~2.0 cm²), a Pt foil as the counter electrode and a Ag/AgCl electrode as the reference electrode. Mixed solution of Na₂SO₃ (0.35M) and Na₂S (0.25M) was used as electrolyte. A 150 W Xenon lamp (Spectra Physics) coupled with an AM 1.5G filter (Newport) was utilized as the simulated sunlight source and to remove light of wavelength below 420nm. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of $10^{-1}$ to $10^{5}$ Hz with an AC voltage amplitude of 10 mA at a DC bias of 0V vs. Ag/AgCl.¹⁷

5.2.4 Photoreduction of CO₂

Photocatalytic reduction of CO₂ in the presence of H₂O was carried out in a lab bench reactor (volume, ~400 mL) with a quartz window on the top of the reactor. The light source was a 300 W Xe lamp. The photocatalytic reaction was performed in a gas (vapor)-solid upper region of the reactor. Liquid water with a volume of 4 mL was pre-charged in the bottom of the reactor. It should be noted that the catalyst was not immersed into the liquid water. Instead, the catalyst was surrounded by H₂O vapor and CO₂. The pressure of CO₂ was typically regulated to 1 atm. The photocatalytic reaction was typically performed for 6 h. The amounts of CH₄ formed were analyzed by gas chromatography. We adopted a flame ionization detector (FID) for quantifying the
amounts of CH\textsubscript{4} formed from CO\textsubscript{2} to ensure high sensitivities. Argon was used as the carrier gas. We performed the same experiment (including both reaction and detection) for at least 3 times for each catalyst, and the relative error was <5\%.\textsuperscript{17}

5.3 Results

5.3.1 Characterization of AEM@GeZnS

AEM@GeZnS chalcogenide material was chosen as the photocatalyst since this particular open framework cluster exhibits high chemical and thermal stability, as well as a suitable band gap and band gap position for CO\textsubscript{2} reduction.\textsuperscript{17b} The solvothermal reaction of Zn(NO\textsubscript{3})\textsubscript{2}, GeO\textsubscript{2}, and sulfur was processed in N-(2-aminoethyl)morpholine (AEM) at 190°C for 12 days, followed by washing with MeOH and CH\textsubscript{2}Cl\textsubscript{2} a few times and activated in a vacuum at room temperature. Large light-yellow rhombic-dodecahedral crystals of AEM@GeZnS were obtained.

Figure 5-4 Thermogravimetric analysis (TGA) of AEM@GeZnS
The AEM@GeZnS crystal was analyzed by powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), Energy-dispersive-X-ray (EDX) spectroscopy, Elemental analysis (EA) and inductively coupled plasma (ICP). This chalcogenide cluster demonstrated exceptional stability in UV light irradiation (6 hours) and thermal stability (250ºC for 6 hours), and the PXRD observed no framework degradation during these treatments. TGA analysis also confirmed that there was no significant weight loss observed before 250ºC, and the framework started to collapse at 600ºC. Combination of single crystal data with ICP, EA, TGA and EDX analysis suggested the overall formula of (AEM)\textsubscript{1.6}@Ge\textsubscript{3.2}Zn\textsubscript{0.8}S\textsubscript{8} for chalcogenide cluster.\textsuperscript{17b}

5.3.2 Ion-exchange

For the AEM@GeZnS structure, protonated AEM (H\textsuperscript{+}-AEM) was incorporated with a negative framework host of zinc-germanosulfide. For obtaining the metal doped cluster, protonated AEM in the cavities could be exchanged with metal cations such as Au\textsuperscript{3+} and Pd\textsuperscript{2+} through the ion exchange treatment. Typically, freshly prepared AEM@GeZnS was soaked in aqueous (or methanol) of metal salt for 3 days. The crystals were then filtered and washed several times with MeOH to remove residual impurities on the surface. The PXRD analysis of Au@GeZnS and Pd@GeZnS confirmed that the exchanged samples still remain highly crystalline with no framework degradation during the ion-exchange process.

The successful incorporation of Au\textsuperscript{3+} and Pd\textsuperscript{2+} cations in the GeZnS structures was confirmed by ICP measurements. The ICP data showed the molar ratio of Au:Zn is 1:5.8
and Pd:Zn is 1: 4.1 for Au@GeZnS and Pd@GeZnS respectively. Additionally, the presence of Au$^{3+}$ in Au@GeZnS was confirmed using EDX analysis, and elemental mapping of scanning electron microscopy (SEM) showed uniform distribution of Au$^{3+}$ on the Au@GeZnS cluster. Moreover, solid-state diffuse reflectance UV/vis spectra were performed on the samples of metal-doped clusters. The band gaps determined using Kubelka–Munk methods are 2.8, 2.6 and 2.5 eV for AEM@GeZnS, Au@GeZnS and Pd@GeZnS, respectively.

Figure 5-5 PXRD of Simulated of AEM@GeZnS, AEM@GeZnS, Pd@GeZnS and Au@GeZnS.
5.3.3 Photoelectrochemical response of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.

To further investigate the semiconducting properties of these open framework clusters, PEC measurements were conducted, using 100 mWcm$^{-2}$ simulated sunlight illumination from a 150 W Xenon lamp coupled with an AM 1.5G filter. Photoanodes were then fabricated using direct current electro deposition to modify a F-doped SnO$_2$ (FTO) electrode with a layer of ground cluster samples.\textsuperscript{17a,18} PXRD and energy-dispersed X-ray spectroscopy (EDX) showed no morphology nor phase change during the electro deposition process. The photocurrent trace of Figure 3a shows rapid response and good reproducibility for all electrodes for numerous on-off cycles under the light on and light off conditions. The photocurrent density of the Au@GeZnS electrode is almost five fold that of AEM@GeZnS and two times that of Pd@GeZnS. Higher photocurrent density indicates better generation and separation of photoinduced electron/hole pairs.

![Figure 5-6 Transient photocurrent density versus time plotted for the electrodes functionalized with the ground materials of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.](image)

Figure 5-6 Transient photocurrent density versus time plotted for the electrodes functionalized with the ground materials of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.
5.3.4 Electrochemical impedance spectra (ESI) of AEM@GeZnS, Pd@GeZnS and Au@GeZnS.

Electrochemical impedance spectra (ESI) of Au@GeZnS and Pd@GeZnS were compared with AEM@GeZnS in dark and illumination conditions. The radiuses of arcs of Nyquist plots shown in figure 5-7 are associated directly with the charge-transfer process. Because the arc radius under illumination is smaller than that in the dark (figure 5-7a), this indicated that the charge-transfer resistance was reduced under irradiation condition for all the photoelectrodes. Moreover, the metal-doped GeZnS based electrodes show a much smaller radii of the semicircle than does the AEM@GeZnS electrode both in the dark and under irradiation. The ESI data demonstrated a better charge transfer process and a more effective separation of photo-generated electron-hole pairs for Au@GeZnS and Pd@GEZnS materials compared with that of AEM@GeZnS.

Figure 5-7 (a) Nyquist plots of the three electrodes in dark, (b) and at present of light.
5.3.5 Photocatalyst result

Generally, CO\textsubscript{2} in the presence of water vapor can be photoreduced to CH\textsubscript{4} using semiconductors such as TiO\textsubscript{2}, Zn\textsubscript{2}GeO\textsubscript{4} and ZnAl\textsubscript{2}O\textsubscript{4} as photocatalysts.\textsuperscript{19,20} Here, photoreduction of the CO\textsubscript{2} + with H\textsubscript{2}O vapor was performed in a gas-solid system over AEM@GeZnS, Pd@GeZnS and Au@GeZnS clusters. As shown in figure 3b, the concentration of CH\textsubscript{4} increased almost linearly under UV-Vis irradiation for all above samples. The results showed significant higher photocatalytic activity for Au@GeZnS and Pd@GeZnS than for AEM@GeZnS under the same reaction conditions. These data clearly show that Au and Pd incorporated materials have better photocatalytic activity for CO\textsubscript{2} reduction than of AEM@GeZnS. The control experiment showed that no CH\textsubscript{4} was detected when the same experiment was carried out without photocatalysts or no irradiation.

Figure 5-8 Three cycle experiments of CO\textsubscript{2} photoreduction into CH\textsubscript{4}. Using 0.2 g of photocatalysts (three clusters) under UV-Vis light.
The photoreduction of CO$_2$ over all samples was repeated three times. After each cycle, the reaction vessel was degassed, next CO$_2$ and water vapor was introduced again. These observations indicated that the photocatalysis could still be restored after three cycles.

5.4 Discussion

The photoreduction of CO$_2$ to CH$_4$ involved two major steps: (i) splitting of water to yield hydrogen (H$_2$O$\rightarrow$ $\frac{1}{2}$ O$_2$ + 2H$^+$ + 2e$^-$, $E^0_{ox} =$ 0.82 V vs NHE), which in turn helps in the (ii) reduction of CO$_2$ to CH$_4$ (CO$_2$ + 8H$^+$ + 8e$^-$ $\rightarrow$ CH$_4$ + 2H$_2$O, $E^0_{red} =$ -0.24 V vs NHE). Functionally, to generate hydrogen cations the photocatalyst should have suitable valence band top edge below the reduction potential of O$_2$ generation from H$_2$O and the bottom energy level of the conduction band should be more negative with respect to reduction potential of CO$_2$ to CH$_4$. The band gaps of AEM@GeZnS, Pd@GeZnS and Au@GeZnS were determined to be 2.8, 2.6 and 2.5 eV, respectively, by UV-vis absorption spectra. The position of conduction band of the photocatalyst could be estimated using the Mulliken electronegativity method. The edge of the valence bands ($E_{VB}$) of AEM@GeZnS, Pd@GeZnS and Au@GeZnS were determined to be 2.29, 2.15 and 2.07 V (vs NHE), respectively, which are more positive than $E^0$ (H$_2$O/H$^+$) 0.82V vs NHE). The edge of conduction bands ($E_{CB}$) of AEM@GeZnS, Pd@GeZnS and Au@GeZnS were estimated to be -0.51, -0.45 and -0.43 V (vs NHE), respectively, which are more negative than $E^0$ (CO$_2$/CH$_4$) (-0.24 vs NHE). These results demonstrate that electrons and holes photogenerated from the photocatalyst clusters can react with absorbed CO$_2$ and H$_2$O to produce CH$_4$. Figure 3b indicates the CH$_4$ evolution over
various photocatalytic samples under UV-Vis irradiation. The metal-doped clusters such as Pd@GeZnS and Au@GeZnS show higher activity toward CH$_4$ formation, a fact that might be attributed to the following two factors: 1. Incorporation of metals cations such as Pd$^{2+}$ and Au$^{3+}$ in the channel of chalcogenide cluster can narrow the band gap. A smaller band gap indicates that more light energy can be absorbed to drive the CO$_2$ photoreduction, thus contributing to an improved photocatalytic performance.\textsuperscript{23} 2. As the PEC measurement demonstrated, the incorporation of Pd$^{2+}$ and Au$^{3+}$ in the framework provides higher electrical conductivity and higher current density.\textsuperscript{17} These increases could improve the separation of photogenerated electrons and holes and lower electron-hole recombination rate, further enhancing photocatalytic activity.

**5.5 Conclusion**

In conclusion, open-framework chalcogenide such as AEM@GeZnS have been demonstrated to be efficient photocatalysts for reduction of CO$_2$ to CH$_4$. We have shown that incorporated samples such as Au@GeZnS and Pd@GeZnS can be prepared using ion-exchange treatment and these materials exhibit high optical and photocatalytic properties. The unique advantages of porous clusters, such as high thermal and high light stability as well as tunable band gaps, provide new opportunities that can be explored to maximize photocatalytic efficiency.
5.6 References


Chapter 6

Appendix

In this chapter, we provide more data, figure and information for supporting the chapters 2, 3, 4 and 5.

Figure 6-1 PXRD of Simulated of ZrPF (Black), ZrPF (blue) and [FeFe]@ZrPF (red).
Figure 6-2 TGA of ZrPF (black) and [FeFe]@ZrPF (red).

Figure 6-3 FTIR spectrum of heterogeneous catalyst [FeFe]@ZrPF upon exposure to visible light. Catalyst before exposure to visible light (Black) and after exposure to visible light for 40 mins (red)
Figure 6-4 The possible mechanism [FeFe]@ZrPF photocatalyst.

Figure 6-5 The pure Complex 1 [(i-SCH2)2NC(O)C5H4N]-Fe2(CO)6 after sublimation
Figure 6-6 XRD patterns for the Fe/N/S-C-4.

Figure 6-7 N\textsubscript{2} adsorption-desorption isotherms of Fe/N/S-C-6.
Figure 6-8  Pore size distribution of Fe/N/S-C-0 and Fe/N/S-C-4.

Figure 6-9  SEM image of Fe/N/S-C-0
Figure 6-10 SEM image of Fe/N/S-C-6.

Figure 6-11 SEM image of hemoglobin after carbonaztion procees no TCA or MS
Figure 6-12 SEM image of the Ti$^{3+}$-TiO$_2$.

Figure 6-13 SEM image of the Ti$^{3+}$-TiO$_2$. 
Figure 6-14 SEM image of the Ti$^{3+}$-TiO$_2$.

Figure 6-15 SEM image of AEM@GeZnS
Figure 6-16 EDX of AEM@GeZnS

Figure 6-17 EDX of Au@GeZn